VOL. XXXIX 1921

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XXXIX

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THIRTY-NINTH GENERAL MEETING

ATLANTIC CITY, N. J.

APRIL 21, 22 AND 23, 1921

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

AT THE OFFICE OF THE SECRETARY

LEHIGH UNIVERSITY, BETHLEHEM, PA.

1922

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VOLUME XXXIX 1921

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE THIRTY-NINTH GENERAL MEETING OF THE SOCIETY, HELD AT ATLANTIC CITY, N. J., APRIL 21, 22 AND 23, 1921.

The registration at this meeting was 104 members and 61 guests, or a total of 165.

PROCEEDINGS OF WEDNESDAY, APRIL 20

Registration began at 6:00 P. M. on the ground floor of the Chalfonte Hotel.

PROCEEDINGS OF THURSDAY, APRIL 21

President W. S. Landis called the Thirty-ninth General Meeting of the Society to order at 9:30 A. M. and after a few introductory remarks asked Dr. Colin G. Fink to act as chairman of the "Corrosion Symposium," which constituted the technical program for the opening session and part of the following morning. In order to cover the very comprehensive program arranged the presentation and discussion of papers by the following authors was at once started: Wm. H. Walker, D. M. Buck, A. S. Cushman and G. W. Coggeshall, W. D. Richardson, F. N. Speller, B. G. Worth, J. A. Aupperle and D. M. Strickland, T. S. Fuller, O. W. Storey, E. A. Richardson and L. T. Richardson. All these papers are printed in full in these Transactions, together with their discussions.

An innovation at this Society meeting took the form of Competitive sports and recreations; the afternoons of Thursday and

Friday having been given over entirely to these events. Through the courtesy of Mr. Frank Hodson the members enjoyed the hospitality of the Sea View Golf Club, which offered exceptional opportunities for golf. The attractive prizes arranged by the Sports and Recreations Committee, with Mr. A. E. Gibbs as Chairman, made the events doubly interesting.

At 6:30 P. M. the Board of Directors of the Society held a dinner meeting in the Chalfonte Hotel for transacting the regular business of the Society.

In the evening the President called upon Mr. H. C. Parmelee to introduce the speaker Dr. R. B. Moore of the U. S. Bureau of Mines. Mr. Parmelee in part spoke as follows:

Mr. Parmelee: A few years ago, in Denver, when the U. S. Bureau of Mines established an office in that city, they sent out a man who was a specialist in the rarer gases of the atmosphere to take charge of that office. I had the pleasure of making his acquaintance shortly after he arrived there, and he did a great favor in showing me a number of these rarer gases. He had them in tubes, and strange to say, they all looked alike. I had no idea whether he was telling the truth or not, when he said this was krypton, this was xenon and this was helium, etc., because, as far as I was concerned, they had the same appearance. Dr. Moore has separated these rare gases from the atmosphere and produced them in as large quantities as possible, and he has had a rather intimate experience particularly with one, namely, helium, recovered from gas wells in Texas.

Dr. Moore's lecture in condensed form is printed in these Transactions.

PROCEEDINGS OF FRIDAY, APRIL 22

At 9:30 A. M. President Landis opened and presided over the annual business meeting of the Society. The minutes of the previous meeting were accepted as printed. The annual report of the Board of Directors, including those of the Secretary and Treasurer were read by Secretary Richards. The reports were approved and are appended to the Proceedings.

In the absence of Dr. Baekeland, Chairman of the Patent Com-

mittee, Mr. C. Bonifant Hamilton, examiner of patents in the U. S. Patent Office, addressed the members in the following words:

C. Bonifant Hamilton: It is my duty in the Patent Office to examine applications for patents in electrochemical arts, particularly those applications pertaining to the various branches of electrolysis. It may be appropriate at this time to lay before this meeting certain of the conditions now existing in the office, as viewed by one within, as an explanation of the delay in receiving actions and the possibly rather poor quality of these actions which those who have, or who have had, application before the office may have noted.

This condition is due primarily to the great quantity of work before the office. It is true that the number of applications involving electrolysis is at present rather small, so that with from fifteen to twenty actions on applications per week the outgo and income of these applications are about equal in numbers. But the work on the remaining desks in the division with which I am associated is very heavy. This applies especially to the alloy, ferrous and non-ferrous metallurgy, electric welding and electric furnace arts.

As many of those present probably know, the situation in the office is also rather critical owing to resignations from the force and the difficulty in getting competent men to come in to fill the vacancies. The entrance salaries are low, advancement is not rapid, and with better prospects outside, the Patent Office at the present time is serving practically only as a training school for those who wish to get training and experience in patent work. Bills have been introduced in Congress for the purpose of granting some relief to both the examining and clerical forces, but the relief measures have all so far failed of passage in both legislative branches.

In view of the conditions now existing within the Patent Office, in view of the fact that the industries of the country are so largely dependent upon the efficiency of the patent system for their growth and development, it is to be hoped that, for the benefit of these industries, relief to the office may be granted before much longer and while it may be that present depressed business conditions have somewhat lessened the rate of resignations from the force, this lessened rate of resignations will not continue and

the quality of the work will of necessity continue to depreciate unless relief of some kind is soon afforded.

J. W. Richards: The new bill which has been introduced into the present Congress is without the rider which was attached to the old bill, and I can say for Mr. Prindle, a member of the Patent Office Committee of our Society, that he hopes the members will back, to the extent of their influence, this new bill because it really gives to the Patent Office needed relief without the vicious rider which was attached to the Nolan patent bill.

Changes in the Constitution which were originally proposed over the signatures of ten members and then revised by the Board of Directors, were unanimously adopted in the form recommended by the Board. The complete Constitution and By-Laws, containing these amendments, is published in these Proceedings.

In the absence of the Tellers of Election, the Chair opened and read the following:

REPORT OF TELLERS OF ELECTION

Following is a list of votes cast in the election of officers for the year 1921-1922:

President: Acheson Smith, 233; L. E. Saunders, 73; J. V. N. Dorr, 46.

Vice-Presidents: C. F. Burgess, 290; C. G. Schluederberg, 181; E. L. Crosby, 168; F. J. Tone, 143; W. H. Walker, 112; Lawrence Addicks, 101; W. R. Mott, 30; J. V. N. Dorr, 1.

Managers: Carl Hering, 287; J. V. N. Dorr, 243; F. A. J. FitzGerald, 189; F. J. Tone, 184; C. E. Skinner, 80; W. H. Walker, 48.

Treasurer: Pedro G. Salom, 340; J. W. Richards, 1.

Secretary: J. W. Richards, 334; H. B. Coho, 1; W. R. Mott, 1; G. A. Roush 1; P. G. Salom, 1; A. T. Hinckley, 1; H. C. Parmelee, 1.

Signed:

Barry MacNutt
Allison Butts
S. S. Seyfert

The President announced the following elections, as the result of the report of the Tellers:

President: Acheson Smith.

Vice-Presidents: C. F. Burgess, C. G. Schluederberg, E. L. Crosby.

Managers: Carl Hering, J. V. N. Dorr, F. A. J. FitzGerald.

Treasurer: Pedro G. Salom.

Secretary: Jos. W. Richards.

At the conclusion of the business meeting the retiring President, Mr. Walter S. Landis, opened the technical session with an address entitled "Our Inventory". This was followed by a continuation of the "Corrosion Symposium" of the previous morning. The contributions were by O. P. Watts and H. C. Knapp, John F. Thompson, H. A. Gardner, H. S. Rawdon, E. R. Shepard, O. P. Watts. This completed the "Corrosion" papers and was succeeded by papers from O. H. Eschholz, Carl Hering. All of these papers with ensuing discussions are printed in full in these Transactions.

On Friday afternoon the golf tournament of the previous afternoon was continued to determine the Society golf championship. For the benefit of those not participating in golf a yachting trip along the beach front was arranged by the Sports and Recreations Committee. With only a few exceptions the members of this party were adjudged good sailors.

On Friday evening several illustrated lectures proved most interesting to those gathered in the auditorium of Haddon Hall. Dr. Fink with the aid of lantern slides addressed the Society on the operation and developments of the Chile Exploration Company's copper extraction plant at Chuquicamata, Chile. President Landis showed slides of the Muscle Shoals nitrate plant of the American Cyanamid Company, which he designed and superintended. Mr. Louis Bond Cherry, of Kansas, illustrated his new gasoline extraction process.

At the conclusion of the exhibition of moving pictures of industrial plants, the prizes were awarded to the winners in the

competitive sports. On this most impressive occasion, Mr. L. E. Saunders made the presentations with appropriate remarks on the skill of the contestants. Mr. J. A. Seede won first prize in the golf tournament through his consistent playing, having netted the lowest score. Messrs. W. M. Corse, C. G. Schluederberg and H. C. Parmelee also won prizes for special distinction in golf. In the "indoor sports", Secretary J. W. Richards won first prize as billiard champion, having defeated G. W. Coggeshall in a closely contested game. The prizes were appropriately arranged for by the committee and generously contributed by the Westinghouse Manufacturing Co., the Haynes Stellite Co., and the Monel Metal Products Corporation.

An informal dance, lasting till midnight, brought the many delightful activities of the day to a close.

PROCEEDINGS OF SATURDAY, APRIL 23

The meeting was called to order at 9:30 A. M. by President Landis. The papers read and discussed were by H. W. Gillett, E. F. Northrup, W. G. Mylius, L. Kahlenberg and W. J. Trautmann, A. W. Laubengayer, Theo. W. Case, S. E. Sheppard, A. S. McDaniel, L. Schneider and A. Ballard, W. A. Noyes, Jr., Wm. Blum, C. P. Madsen, C. W. Hazelett, C. W. Marsh. A paper by T. R. Briggs and W. J. Bartlett, from a previous meeting, was called up for discussion only, having been already printed in Vol. XXXVII. With the exception of the latter the papers with discussion are printed in these transactions.

Dr. Fink then offered the following resolution of thanks, which was unanimously adopted by a rising vote.

Resolution of Thanks

The American Electrochemical Society, closing its Thirty-ninth General Meeting, at Atlantic City, wishes to place on record its cordial appreciation of the assistance and co-operation rendered by the following persons and organizations:

The management of the Hotel Chalfonte and Haddon Hall, for facilities for holding our technical sessions and for the use

of their large assembly hall for exhibition of moving pictures and for dancing.

The Chile Exploration Co., The American Cyanamid Company and Mr. L. B. Cherry, for the use of their moving picture films.

The Sea View Golf Club and the Pleasantville Gun Club, particularly its president, Mr. Roselle, for the generous tendering of the use of their grounds and facilities by our members and guests.

The Westinghouse Electric Company, The Haynes Stellite Company, and the Monel Metal Products Corporation, for generous donation of prizes for the sports competitions.

The Ladies' Committee, for their care of visiting ladies, particularly the untiring service of Mrs. Henry Hess.

The Chairman and members of the Sports Committee, for arranging a pleasing novelty in the program of our Meetings.

The Local Committee in general charge of arrangements, particularly its efficient chairman, Dr. Carl Hering, for the time and thought devoted towards the success of the meeting.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the Members of the American Electrochemical Society:

The following are some of the important items of business transacted by your Board of Directors during the past year:

The Society appropriated 187.5 francs to the International Chemical Union and thus became a participant in its activities.

Messrs. Carl Hering, F. C. Frary and Lawrence Addicks were appointed a committee on Insulation, to co-operate with a similar committee of the National Research Council and also with similar committees from the American Institute of Electrical Engineers, American Physical Society, American Chemical Society, National Electric Light Association and Council of Electrical Manufacturers, all working under the leadership of the Engineering Division of the National Research Council.

A referendum of the members of the Society on the resolution concerning the adoption of the metric system resulted in 483 members in favor of its adoption as the only legal system of

weights and measures in the United States and 107 members opposed. The Board voted to simply transmit a statement of the result of the referendum, without comments, to the American Metric Association.

Mr. Acheson Smith, President of the Electric Furnace Association, having proposed the affiliation of that association with the American Electrochemical Society, which would include the formation of an Electric Furnace Section of the Society, the Board met the proposition by drawing up a By-Law covering divisions of the Society, the result of which has been the circularization of the Society for members enrolling in the Electrothermic Division.

At the December Meeting of the Board, Messrs. Acheson Smith (Chairman), C. F. Burgess, Carl Hering and C. G. Schluederberg were appointed a committee to report on "Policy" to the Board of Directors. The result of this committee's work is seen in the Amendments to the Constitution, which were being voted upon at this meeting.

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: In 1920 the Society held two general meetings, one in Boston and Cambridge, April 8th to 10th, at which the attendance was 149 members and 124 guests, total 273; the second at Cleveland, September 30th to October 2nd, at which the registration was 105 members and 80 guests, total 185. The Transactions of the Spring Meeting include 43 papers, and those of the Fall Meeting, 17 papers.

During November of last year Volume XXXVI was distributed to members. Volume XXXVII, containing 744 pages was distributed in March of this year.

The edition of Volume XXXVI was as follows: 1,650 copies complete, bound in cloth, 350 copies bound in paper for distribution to the Faraday Society, 250 copies unbound to be kept in stock, and 50 extra copies of each paper, with discussion, for distribution in pamphlet form to authors of papers.

The edition of Volume XXXVII was as follows: 1,650 copies complete, bound in cloth; 350 copies bound in paper for distribution to the Faraday Society; 250 copies unbound to be kept in stock, and 50 extra copies of each paper, with discussion, for distribution in pamphlet form to authors of papers.

The stock of Volumes on hand December 31, 1920, was as follows:

Volume I, 74 Copies; II, 106; III, 13; IV, 267; V, 217; VI, 249; VII, 198; VIII, 339; IX, 331; X, 265; XI, 289; XII, 259; XIII, 212; XIV, 492; XV, 336; XVI, 389; XVII, 588; XVIII, 591; XIX, 462; XX, 429; XXI, 486; XXII, 428; XXIII, 464; XXIV, 497; XXV, 495; XXVI, 520; XXVII, 418; XXVIII, 507; XXIX, 141; XXX, 459; XXXI, 99; XXXII, 332; XXXIII, 305; XXXIV, 262; XXXV, 666; XXXVI, 617; Index, 516.

Financial Statement

Receipts in 1920.

Cash Assets, beginning January, 1920, account		$ 4,121.39
Entrance Fees	$1,685.10	
Current Dues	9,169.31	
Volumes 1920	5,353.40	
Back Dues	665.00	
Volumes 1919	300.00	
Advance Dues, 1921	1,855.00	
Advance Dues, 1922	5.00	
Volumes 1921	1,125.00	
Volumes 1922	5.00	
Sale of Publications	2,069.87	
Sale of Reprints	760.90	
Sale of Membership Certificates	12.00	
Sale of Society Pins	10.50	
Payment for 1918 Transactions by Faraday Society	191.25	
Subscription to Faraday Society Transactions	320.00	
Interest on Liberty Bonds	425.00	
Interest on Philadelphia Electric Bonds	155.00	
Interest on Philadelphia Bank Account	60.07	
Interest on Local Bank Account	56.49	
		$24,223.89
		$28,345.28

EXPENDITURES IN 1920.

Secretarial Appropriation	$ 3,600.00	
Office Printing	682.20	
Printing of Volume 35	3,496.36	
Printing of Volume 36	4,270.19	
Printing of Volume 37	1,952.03	
Printing of Volume 38	394.78	
Printing of Discussions—Vol. 36	1,297.24	
Preprints for Volume 37	4,425.35	
Preprints for Volume 38	1,349.50	
Engraving	441.75	
Extra Reprints	627.78	
Binding of Back Volumes	113.50	
Office Postage	456.12	
Postage on Advance Copies and Bulletins	1,275.00	
Express and Postage on Volumes	369.02	
Office Expenses	1,473.88	
Expenses of Meetings	1,096.17	
Office Equipment	81.30	
Storage and Insurance	255.33	
Membership Committee	2.16	
Publication Committee	10.09	
Booth Committee	74.75	
Local Sections	300.00	
Dues to International Chemical Union	13.42	
Contribution to "Annual Tables of Physical and Chemical Constants"	75.00	
		$28,132.92
Cash Assets, Beginning January, 1921, Account		212.36
		$28,345.28

Condition of Membership of the Society in 1920.

Members January 1, 1920		2,209
Elected and qualified as members in 1920		381
		2,590
Deaths in 1920	22	
Resignations in 1920	75	
Dropped for non-payment of dues in 1920	129	
		226
Members December 31, 1920		2,364
Net increase for calendar year		155

Condition, April 21, 1921.

Members January 1, 1921		2,364
Qualified as members to April 21, 1921		50
		2,414
Deaths	1	
Dropped for non-payment of dues	108	
		109
Members April 21, 1921		2,305
Members April 7, 1920		2,307
Net decrease		2

TREASURER'S ANNUAL REPORT, 1920.

January 1, 1920, cash balance	$ 4,121.39	
Total receipts for 1920	24,223.89	
		$28,345.28
Total expenditures, 1920		28,132.92
Balance, December 31, 1920		$ 212.36
Balance in Commonwealth Trust Co., 12-21-20	$ 174.78	
Balance in E. P. Wilbur Trust Co., 12-21-20	3,927.94	
Balance in Cash Drawer	50.00	
		$ 4,152.72
Less December, 1920, checks not in		3,940.36
Balance 12-31-20 as above		$ 212.36

We have examined the above statement of account, and receipts and expenditures for the year 1920, and find the same to be correct.

We also report the following securities of the Society in the Safe Deposit Vault of the Commonwealth Title Insurance and Trust Co., Philadelphia, Pa.:

Philadelphia Electric Co. 5's	$ 3,100.00
1st Liberty Loan	2,000.00
2d Liberty Loan	2,000.00
3d Liberty Loan	2,000.00
4th Liberty Loan	2,000.00
5th or Victory Loan	2,000.00
	$13,100.00

(Signed) CARL HERING,
(Signed) S. S. SADTLER,
Auditors.

MEMBERS AND GUESTS REGISTERED AT THE THIRTY-NINTH GENERAL MEETING

Members.

F. Anderson
W. H. Arison
Wm. W. Atkinson
J. A. Aupperle
T. F. Baily
R. L. Baldwin
W. D. Bancroft
W. J. Beck
E. O. Benjamin
W. H. Bennett
Wm. Blum
F. W. Brooke
D. M. Buck
L. J. Buck
C. F. Burgess
D. C. Burroughs
Gustav Carlsson
L. B. Cherry
Richard B. Chillas
G. H. Clamer
G. W. Coggeshall
E. F. Cone
W. M. Corse
W. A. Cowan
C. A. Crawford
E. L. Crosby
A. S. Cushman
F. W. Davis
J. V. N. Dorr
O. H. Eschholz
C. Fineman
Colin G. Fink
F. A. J. FitzGerald
J. A. Fogarty
W. R. Forrester
J. J. Frank
W. H. Fulweiler
A. E. Gibbs
C. B. Gibson
Helen C. Gillette
H. M. Goodwin
A. K. Graham
John E. Han
Carl Hering
Henry Hess
A. T. Hinckley
Frank Hodson
Karl Horine
Neil Hume
H. M. Johnquest
Lyman C. Judson
F. T. Kaelin
J. Kelleher
H. W. Kellogg
F. R. Kemmer
Ivar Kenway
W. S. Landis
W. T. Little
R. A. Long
H. S. Lukens
Einar Lund
J. Y. McConnell
A. S. McDaniel
H. S. McQuaid
H. S. Miner
Wm. C. Moore
E. F. Northrup
H. C. Parmelee
Charles L. Parsons
E. C. Pitman
L. A. Pratt
D. C. Reed
R. E. F. Rhodin
Jos. W. Richards
L. T. Richardson
W. D. Richardson
E. G. Rippel
Chas. Robbins
C. J. Rodman
D. A. Russell
L. E. Saunders
C. G. Schluederberg
J. A. Seede
Acheson Smith
W. S. Smith
F. N. Speller
A. D. Spillman
H. M. St. John
F. G. Stantial
M. E. Stewart
H. Styri
Walter T. Taggart
Sterling Temple
F. J. Tone
M. Unger
C. H. Vom Baur
C. J. Wernlund
R. H. White
Dudley Willcox
H. M. Williams
A. M. Williamson
Chas. Wirt
B. G. Worth
J. C. Wright
R. E. Zimmerman

Guests.

S. B. Applebaum, New York City
Mrs. E. O. Benjamin, Newark, N.J.
A. F. Braid, New York City
Mrs. A. F. Braid, New York City
Bennett Chapple, Middletown, O.
Mrs. L. B Cherry, Kansas City, Mo.
H. E. Clifford, Boston, Mass.
G. F. Creveling, New York City
B. S. Cushman, Auburn, N. Y.
R. B. Dimmick, Canton, O.
W. H. Falck, Chicago, Ill.
Irving Fellner, New York City
Mrs. Colin G. Fink, S. Yonkers, N. Y.
Wm. H. Finkeldey, Palmerton, Pa.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
T. S. Fuller, Schenectady, N. Y.
J. S. Gates, Philadelphia, Pa.
I. N. Goddard, Atlanta, Ga.
Mrs. V. P Hamilton, Washington, D. C.
B. Hamilton, Washington, D. C.
Mrs. Henry Hess. Atlantic City, N. J.
Carl D. Hocker, New York City
W. E. Holmes, Washington, D. C.
C. J. Holslag, Newark, N. J.
G. S. Houghland, Parlin, N. J.
Mrs. G. S. Houghland, Parlin, N. J.
Samuel L. Hoyt, Cleveland, O.
T. M. Hunter, Newark, N. J.
Mrs. H. W. Kellogg, Niagara Falls, N. Y.
Stem Kinman, York, Pa.
F. W. Knowles, Portsmouth, O.
H. Kriegsheim, New York City
Wm. J. Latta, Wheeling, W. Va.
Miriam McConnell, Phila., Pa.
R. J. McKay, Pittsburgh, Pa.
Geo. P. Mills, Philadelphia, Pa.
Miss Lillian Moore, Baltimore, Md.
Miss Mary Moore, Nashville, Tenn.
R. B. Moore, Washington, D. C.
Mrs. R. B. Moore, Washington, D. C.
Thomas Moore, Baltimore, Md.
Mrs. Wm. C. Moore, Baltimore, Md.
W. G. Mylius, Wilkinsburg, Pa.
Jas. A. Newlands, Hartford, Conn.
Mrs. S. Northrup, Princeton, N. J.
Mrs. E. C. Pitman, Parlin, N. J.
M. B. Rascovich, New York City
H. S. Rawdon, Washington, D. C.
A. C. Recker, Waterbury, Conn.
James Q. Rice, New York City
Chas. A. Schnaischn, Pittsfield, Mass.
T. Smith, Waterbury, Conn.
D. M. Strickland, Middletown, O.
C. G. Stupp, Cliffside, N. J.
J. F. Thompson, New York City
C. A. Timmons, New York City
H. M. VanDeusen, New York City
C. A. Ward, New York City
Mrs. A. M. Williamson, Niagara Falls, N. Y.
Mrs. M. A. Wirt, Germantown, Philadelphia, Pa.

CONSTITUTION, BY-LAWS AND SUNDRY REGULATIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

CONSTITUTION

Article I.

Name and Objects.

1. The name of this association shall be the American Electrochemical Society.

2. Its objects shall be the advancement of the theory and practice of Electrochemistry, Electrometallurgy, Electrothermics and allied subjects. Among the means to this end shall be the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions and communications as may seem expedient, and coöperation with chemical, electrical and other scientific and technical societies.

Article II.

Membership.

1. The membership shall consist of members and honorary members.

2. The only requirement for eligibility to nomination as member is that the candidate shall be interested in the subject of electrochemistry.

3. Honorary members shall be those who by reason of valuable contributions to electrochemistry deserve special recognition by the Society.

Article III.

Admission and Dismissal of Members.

1. Those who have, prior to April 6, 1902, notified the proper authorities that they wish to become members of the Society, are by the adoption of this constitution elected as charter members.

They shall not be required to pay an entrance fee; they shall, however, be required to pay their dues for the current year within three months.

2. Application for admission after April 6, 1902, shall be made in writing in a form prescribed by the Board of Directors, and shall refer to at least two members. If the applicant is unable to do this he shall refer to at least three persons, including their address, of reputable standing, preferably electrochemists, chemists, electrical engineers, professors or instructors in institutions of learning. The application shall also state the present occupation of the applicant, and briefly in what capacity he is interested in the subject of electrochemistry.

3. The Assistant Secretary shall send to each director, at least twenty days before an election, the names and addresses of the applicants and their respective references, provided the applications are in due form. The Board of Directors at a duly called meeting shall consider such applications. The election to membership shall be by a vote of the Board of Directors at that or at a subsequent meeting. Proxy votes shall be included; also mail votes received before the election. Two negative votes shall exclude a candidate. The Board of Directors may refuse to elect a candidate whose character, reputation, or professional conduct would make him, in the opinion of the Board of Directors, an undesirable member. The names of those only who have been elected shall be announced to the Society. A candidate who has been duly elected shall be placed on the rolls and have all the rights and privileges of a member as soon as his entrance fee and dues for the current year have been paid.

4. A member desiring to resign shall send a written communication to the Secretary, who shall accept and announce the resignation provided the dues and other indebtedness of that member have been paid to the mailing of his resignation.

5. Upon the written request of ten or more members that, for cause stated therein, a member be dismissed, the Board of Directors shall consider the matter, and if there appears to be sufficient reason, shall advise the accused of the charges against him. He shall then have the right to present a written defense, and to appear in person before a meeting of the Board of Direc-

tors, of which meeting he shall receive notice at least twenty days in advance. Not less than two months after such meeting, the Board of Directors shall finally consider the case, and if in the opinion of the majority of the Board of Directors a satisfactory defense has not been made, and the accused member has not in the meantime tendered his resignation, he shall be dismissed from the Society.

6. Honorary members shall be recommended over the signatures of at least ten members, and shall be elected only at the meeting of the Board of Directors in conjunction with a general meeting of the Society, and by the unanimous vote of the Directors present, a quorum being present.

Honorary members shall pay no entrance fee or annual dues, and shall receive all the Publications of the Society.

The number of honorary members shall not at any time exceed ten, and not more than two shall be elected in any one calendar year.

Article IV.

Dues

1. The entrance fee, payable on notification of election, shall be five dollars. If not paid within three months after notification, the election of the applicant is thereby canceled. Applicants for membership who are at the date of their election students in attendance at colleges, universities and technical institutions, shall be exempted from payment of the Entrance Fee.

2. The annual dues shall be five dollars. They shall be due at the beginning of the calendar year, and notice thereof shall be mailed to each member before the end of the preceding year. If not paid before the sixteenth day of March, the delinquent member shall lose his right to vote or to receive the publications of the Society, until said dues are paid. Members will pay dues for, and receive the publications of, the year in which they are elected, but if elected within two months of the end of the calendar year may, at their option, pay for, and enter with the next coming year.

3. Any member who, at the sixteenth day of March, is in arrears for two years shall be dropped from the rolls, and shall not be included in subsequently published lists of members. The

Board of Directors may reinstate a member who has been dropped, provided all his arrears have been paid.

Article V.

Officers.

1. The Officers of the Society shall be a President, six Vice-Presidents, nine Managers, a Secretary, and a Treasurer, who shall hold office as follows:

2. The President, the Secretary, and the Treasurer for one year, the Vice-Presidents for two years, and the managers for three years. At each annual meeting a President, three Vice-Presidents, three Managers, a Secretary, and a Treasurer shall be elected, and their term of office shall begin at the close of the annual meeting. Each officer shall hold office until his successor has qualified.

3. A vacancy in the office of President shall be filled by the senior Vice-President; a vacancy in the office of Vice-President shall be filled by the senior Manager. Seniority between officers of the same rank and date of election shall be determined by the number of votes received when they were elected; or if the same, then by the date of their election to membership, or if this be also the same, then in alphabetical order. All other vacancies shall be filled by the Board of Directors.

4. No officer shall receive, directly or indirectly, any salary, compensation or emolument from the Society, either as such officer or in any other capacity, or be interested, directly or indirectly, in any contract relative to the operations conducted by the Society or in any contract for furnishing supplies thereto, unless authorized either by the by-laws or by vote of the majority of the entire Board of Directors.

Article VI.

Election of Officers.

1. Prior to November 1st, the Board of Directors shall appoint a Nominating Committee of five members, not more than two of whom may be Officers of the Society, who shall send to the Assistant Secretary prior to December 1st a list entitled, "Nomi-

nees suggested by the Nominating Committee," containing the names of at least one and perferably several candidates for each office. This list shall be printed on the nominating blanks under the prescribed title.

The Assistant Secretary shall send to all members nominating blanks not later than the 15th of December, and nominations, upon these forms, will be received by the Assistant Secretary not later than the 15th of January.

2. At the Directors' meeting, held prior to January 15th in each year, the Board of Directors shall appoint three tellers, who shall not be members of the Board of Directors, and three alternates. Should the Directors meeting not be held, the President shall appoint these tellers, who shall be notified by the Assistant Secretary.

3. The tellers shall meet as soon after the 15th day of January as possible. The Assistant Secretary shall deliver to the tellers all nomination ballots received, marking on the outside of the envelopes those received from members not entitled to vote. The tellers shall open only the envelopes not thus marked and shall proceed in secret to count the votes. The tellers shall prepare and sign a report of the results of the vote and deliver it sealed to the Assistant Secretary, who shall deliver it sealed, together with the ballots and the unopened envelopes, to the President at the next meeting of the Board of Directors, or of the Executive Committee, at which it shall be opened and read.

4. The Assistant Secretary shall mail to every member, before February 16, a printed list of all candidates thus nominated who have received more than 5 percent of the number of valid nominating ballots cast; he shall previously, however, give to each of such candidates notification of his nomination, within a week of which notification a candidate may elect to withdraw his name from the voting ballot. The voting need not be restricted to the names on the list. The Board of Directors may endorse those which it prefers, and, if so, the published list shall state it. Both nomination and voting shall be by secret ballot; the voter shall sign his name on an outside envelope, and the ballot shall be enclosed in an inner sealed and unmarked envelope.

Voting ballots must reach the Assistant Secretary before the 16th day of March. The results of the election shall be announced at the annual meeting.

5. The tellers shall meet as soon after the fifteenth day of March as possible. The Assistant Secretary shall deliver to the tellers all ballots received by him, marking the outside envelopes received from members not entitled to vote. The tellers shall open only the envelopes not thus marked, and shall proceed in secret to count the votes received before the sixteenth day of March. All ballots and unopened envelopes shall be returned to the Assistant Secretary, who shall preserve them for one month. At the end of one month the Assistant Secretary shall return to the senders all rejected envelopes and shall open all unidentified envelopes. Cumulative votes shall count as one vote. The tellers shall prepare and sign a report of the results of the vote, which shall be sealed, and shall remain in the possession of the Chairman of the Committee, who shall hand this report to the presiding officer at the ensuing annual meeting. The presiding officer shall then cause this report to be read, and shall declare duly elected the eligible persons receiving the greatest number of votes for the respective offices.

6. At the request of the Board of Directors these tellers shall count the ballots of any mail vote of the Society.

7. The President and Vice-Presidents shall, after the expiration of the full term of office to which they were elected, be ineligible for immediate re-election to the same office.

Article VII.

Management.

1. The affairs of the Society shall be managed by a Board of Directors under this constitution and by-laws. This Board shall consist of the Officers and the immediate Past President. The President, Vice-President, Secretary, and Treasurer of the Society shall hold the same offices in this Board of Directors.

2. The Board of Directors shall prepare and adopt a series of by-laws which shall govern its meetings and its procedure, as also that of the Society under this constitution. It shall require a two-

thirds vote of the whole Board to adopt or amend these by-laws; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed by-laws or amendments shall be furnished to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

3. The Board of Directors may delegate any or all of its powers, except in those cases in which this constitution requires a vote of the whole Board, to an Executive Committee of not less than one-third of the number of members of the Board of Directors. The President and Secretary shall be members of this Executive Committee. This committee shall conduct the affairs of the Board of Directors between its meetings. All members of the Board of Directors shall receive notice of the meetings of this Executive Committee and shall have the right to attend and vote. A majority of the Executive Committee shall constitute a quorum.

4. At the request of the President, matters requiring action by the Board of Directors may be discussed and voted upon by a mail vote of the Board of Directors.

5. The duties of the President, Vice-Presidents and Treasurer shall be such as usually pertain to the offices they hold, besides any others designated in the constitution or by-laws or by the Board of Directors. The Secretary shall be in administrative charge to direct and supervise the duties usually pertaining to this office or designated in the constitution or by-laws or by the Board of Directors; but he shall be relieved of the clerical or other work in executing these duties by an Assistant Secretary, who shall be appointed by the Board of Directors and shall be responsible to the Board. The Secretary shall instruct the Assistant Secretary in his duties, and the work of this Assistant Secretary shall be done under the direct supervision of the Secretary. The Secretary and Assistant Secretary shall in all matters concerning the affairs of the Society carry out the prescriptions of the constitution, by-laws, rulings and precedents, and in cases in which no such prescriptions exist they shall obtain decisions from the Board of Directors or Executive Committee, or if time does not permit they shall confer with the President. All funds expended

in the Secretarial duties shall be under the control of the Secretary who shall be responsible to the Board of Directors for the proper dispensing of such funds. The Secretary and the Treasurer shall present reports annually to the Board of Directors before the annual meeting. The Board of Directors shall present a report annually to the Society at the Annual Meeting, the material for such report shall be prepared by the Assistant Secretary under the direction of the Secretary. The nature of these reports shall be specified in the by-laws.

6. All standing committees shall be directly responsible to the Board of Directors, and shall be appointed by the President or by the Board of Directors.

Article VIII.

Meetings.

1. The annual meeting shall be held during the last week of March or in April. Business affecting the organization of the Society shall be transacted only at the annual metings. Proxy or mail votes shall be received.

2. Other meetings may be held at such times and places as the Board of Directors shall select. The President shall call a meeting at the written request of 30 or more members.

3. Notice of all ordinary meetings shall be sent to all members at least twenty days in advance, and of the annual meeting, thirty days in advance.

4. Any ten members at a meeting of the Society may require that any motion brought up be referred to a referendum of the Society by a mail vote.

Article IX.

General.

1. A quorum of the Society shall consist of fifty members residing in the United States, present in person or by proxy.

2. Every member entitled to vote at any meeting may vote by proxy or, when the subject-matter has not been changed, by mail. No proxy shall be valid after the expiration of eleven months

from the date of its execution. Every proxy shall be revocable at the pleasure of the person executing it.

3. The fiscal year of the Society shall begin January 1st.

Article X.

Amendments.

Proposals to amend this constitution shall be made in writing to the Board of Directors and signed by at least ten members; they shall reach the Secretary not later than February 1st. The Board of Directors shall consider them and may amend them. The original, with the action of the Board of Directors, shall then be presented to the Society at its annual meeting, at which time it may be further amended. In its final form it is to be voted upon by a mail vote, which is to be taken as soon after the annual meeting as practicable, and which is to be conducted in the same way as prescribed for the election of officers. A majority of the votes cast shall decide.

BY-LAWS

1. *Order of Business.*—At the annual meeting of the Society the order of procedure of the business session shall be as follows:

Reading of the minutes of the last meeting.

Report of the Board of Directors, including those of the Secretary and Treasurer.

Report of Standing Committees.

Deferred business.

New business.

Report of tellers of election.

Address of the retiring president. (This may be deferred to a later session of the general meeting, at the discretion of the framers of the program of the meeting.)

The business meeting of the Society shall preferably be the second day of the annual meeting.

2. *Meetings of the Board of Directors.*—The Board of Directors shall hold a regular meeting immediately preceding each general meeting of the Society, or at the annual meeting at any time before the business meeting of the Society.

Between said meetings the Board of Directors may hold special meetings when called by the President, and coincident with monthly meetings of the Executive Committee when applications for membership are to be acted upon.

At the regular meetings of the Board of Directors the order of procedure shall be as follows:

Reading of the minutes of the last regular meeting and of any special meeting, the minutes of which have not been approved.

Election of new members.

Appointment of tellers of election.

Approval of bills.

Communications from the Secretary.

Communications from the Treasurer.

Communications from the President.

Discussion of program of future meetings of the Society.

Reports of committees.

Deferred business.

New business.

Adjournment.

At special meetings of the Board of Directors, the order of procedure shall include the reading of the minutes of the last meeting of the Board and such other of the above items of procedure in their order given as are to be acted upon.

3. *Duties of Officers.*—The President shall preside at all meetings of the Society and at those of the Board of Directors. He may represent the Society at any function to which no other particular delegate has been appointed by the Society or the Board of Directors. The President (or any director) shall have the power of appealing any action of the Executive Committee to the Board of Directors, within two weeks of its adoption, which action can then be carried into effect only after approval by a majority of the entire Board of Directors voting on said explicit action either in person or by mail ballot. He shall deliver an address at the annual meeting of the Society at which his term of office expires.

The Vice-Presidents, in the order of their seniority, shall assume the duties and responsibilities of the President in case of his death, disability or absence from fulfilling his duties.

The Secretary, besides performing the usual duties of that

office, shall be the guardian of the records of the Society, collect dues from members and all bills owing to the Society, and pay such amounts to the Treasurer. At meetings of the Society he shall collect and receive manuscripts of the papers read, with drawings or diagrams thereto belonging, and shall be responsible for their custody until he hands them to the Publication Committee. He shall report to the Board of Directors at its meeting held at the annual meeting of the Society, on the condition of the affairs of the Society, such as the membership, publications, number of meetings, number of papers read and in general a summary of the work and condition of the Society, excepting its finances, and make such recommendations as he thinks will facilitate the transaction of the business affairs of the Society or in any way advance its interests. It shall be the further duty of the Secretary to organize and maintain means for securing the submission of papers to the Publication Committee.

The Treasurer shall report to the Board of Directors at its meeting immediately preceding the business session of the annual meeting of the Society on the condition of the finances of the Society and make such recommendations as will in his opinion tend to safeguard or improve the same.

The Board of Directors shall report to the annual meeting on the general affairs of the Society, including the abstracts of the reports of the Secretary and the Treasurer and any other matters which they may consider of interest to the Society.

4. Standing Committees. *Publication Committee.*—The Publication Committee shall consist of a Chairman, the President (*ex officio*), the Secretary (*ex officio*) and four members. The Chairman of the Committee, to serve for one year, and two members, to serve for two years, shall be appointed yearly by the incoming President, subject to the approval of the Board of Directors. (In the first instance four members shall be appointed, two to serve for two years, and two to serve for one year.) Retiring members shall be eligible for re-appointment. Vacancies arising on the Publication Committee shall be filled by appointment by the President, subject to the approval of the Board of Directors.

The Publication Committee shall meet at each general meeting

of the Society, at which time it shall set a date prior to which papers for the next meeting may be submitted. It shall pass on all papers so submitted, and shall have complete discretion as to what papers shall be accepted for presentation at the meetings of the Society; provided, however, that any member may appeal to the Board of Directors against any decision of the committee in respect to a paper submitted by that member.

The committee shall deal with all papers submitted as promptly as possible, and shall, where desirable, assist authors by suggestions which would improve the form of their papers as submitted.

No member of the committee shall pass on any paper of his own.

The committee shall have charge of the publication of the Transactions of the Society, and shall decide what papers shall be published in the Transactions. The editing of the Transactions shall be in the hands of the committee.

The committee may assign work in connection with its duties to whatever member of the Society it sees fit.

The Chairman of the Publication Committee shall keep a record of all papers submitted and of the action taken thereon. He shall report to the Board of Directors at each general meeting of the Society, and shall be responsible to the Board for the carrying out of the Committee's duties according to the by-laws.

5. *Quorum of Directors.*—A quorum of the Board of Directors shall be twelve, present in person or by proxy.

6. *Treasurer's Accounts.*—The President shall appoint two auditors, at least one week before the annual meeting, to audit the accounts of the Treasurer. At least one of the said auditors shall be a member of the Board of Directors, and said member shall report the result of said audit to the Board of Directors at its meeting, preceding the annual business meeting of the Society.

7. *Entrance Fees.*—Any entrance fee paid by an applicant shall be returned if the applicant is not elected.

8. *Guests at Meetings.*—Guests may be introduced to the meetings of the Society by members and may be given the privilege of attending the meetings and may be given such further privileges

as may be extended to them by the Local Committee or the President or Secretary.

9. *Membership Committee.*—A Committee on Membership, whose function shall be to enlarge by systematic effort the membership of the Society, shall be appointed annually by the incoming President. It shall consist of 15 or more members.

10. At each annual meeting of the Society at least one session shall be devoted to the subject of Electrothermics.

11. *Divisions.*

Sec. 1. Professional groups, to be known as Divisions of the Society and to be organized from its members, may be authorized by the Board of Directors. Any member of the Society may register for membership in any Division in which he is interested and may resign therefrom at his discretion.

Sec. 2. The officers of the Division shall be a Chairman, one or more Vice-Chairman and a Secretary-Treasurer. The above officers, together with four other members of the Division shall constitute the Executive Committee of the Division. One of the members of the Division Executive Committee shall be chosen from the Board of Directors of the Society and shall, therefore, represent the Division at meetings of the Board of Directors of the Society.

The Division shall elect its officers and other members of the Executive Committee during the annual meeting of the American Electrochemical Society or within thirty days thereafter. The officers and other committee members shall be elected for such terms as the Division By-Laws may provide, these terms of office not to exceed two years unless an individual should be re-elected.

Sec. 3. A Division shall have the right to make rules for its own government, subject to the approval of the Board of Directors, not inconsistent with the constitution and by-laws of the Society. Amendments or additions to these rules shall also be subject to the approval of the Board of Directors.

Sec. 4. A Division shall hold at least one session at one or both of the general meetings of the Society each year, such session to be under the auspices of said Division, and publication of

papers for such sessions, as preprints or in the Transactions of the Society, being subject to the usual regulations and control of the Committee on Publications of the Society.

Sec. 5. The Board of Directors may recommend the dissolution of any Division of the Society, such recommendation to be acted on at annual meeting of the Society.

SUNDRY REGULATIONS

Regulations Concerning the Formation and Conduct of Local Sections.

1. A Local Section of this Society may be authorized by the Board of Directors, at the written request of three members. Only one Section shall be authorized in any one locality.

2. Any member of the Society, in good standing, may enroll as a member of any Local Section, provided he complies with the regulations of the said Section. Only members of this Society are eligible to membership in its Local Sections.

3. The regulations of Local Sections are subject to the approval of the Board of Directors.

4. The expenses of each Local Section shall be borne by the members enrolled in said Section. The Society shall not be responsible for any debts contracted by a Local Section or the officers thereof.

5. The Society will print advance copies of papers offered to Local Sections, in order to facilitate full discussion thereon, provided that said papers are approved for such advance publication by the chairman of the Local Section and by the Publication Committee of the Society.

6. Papers read before Local Sections, and discussions thereon if reported, are to be considered as the property of this Society. They shall be submitted to the Publication Committee of the Society and published in the Transactions if approved by it. Reading of a paper before a Local Section does not carry with it the right of publication in the Transactions.

Papers read before Local Sections may be offered for reading at general meetings of the Society, and will be given equal standing with other papers on the program of said meeting, when approved by the Committee on Papers.

7. The Board of Directors reserves the right to abrogate, amend or add to these regulations, or to pass upon such questions concerning the welfare of Local Sections not covered by these regulations.

8. Each Local Section shall transmit promptly to the Secretary of the Society, an abstract of its proceedings, including the titles and names of authors of all papers read before it, for the purpose of preparing a report to be published in the Transactions of the Society, and for the purpose of enabling the Board of Directors to comply with Articles 3 and 7 of these regulations.

Action of May 2, 1907.

Local Sections of the Society are allowed to draw upon the Society for financial assistance during the current year, to the limiting sum not exceeding $1.00 for each of their members. This money is intended to pay rent for rooms, sending of notices, etc.

[The above action, taken in 1907 for that current year, has been renewed in subsequent years when the Society was able to give Local Sections this assistance.]

RULINGS OF THE BOARD

Acceptance of Papers.

In general, no paper may be presented at a meeting of the Society unless it has been submitted in full prior to a date set by the Publication Committee as suitable to allow consideration by that committee and the printing of advance copies before the meeting. In exceptional cases the President may authorize a paper, not previously submitted to the Publication Committee, to be read; such authorization will not, however, bind the Society or the Publication Committee in any way as to printing or publication.

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Papers of the following classes will be regarded as undesirable:

(a) Those containing no information or obviously incorrect information.

(b) Those containing only information already easily accessible.

(c) Those of an advertising nature not counterbalanced by adequate scientific information and treatment.

Authors' abstracts of papers already published elsewhere may, however, be accepted for the purpose of discussion. Papers already published but not easily accessible will, if otherwise desirable, generally be accepted.

Advance Copies of Papers.

Advance copies of such papers as are accepted by the Publication Committee will be printed as soon as possible for distribution before the meeting, and the author will receive twenty-five of these copies gratis, and have the right to order as many as he may wish at the regular rates.

Discussions.

The Publication Committee will edit discussions; it shall not however, change the meaning of any contributor's remarks, and the revised form of each contributor's remarks will be sent to him for approval; unless objection be raised within one week, it will be assumed that such is approved.

Complete Sets of Transactions.

Complete sets of Transactions of our Society may be obtained by members, at a discount of 25 percent from the published price to members for single volumes, and to public libraries, journals and scientific societies at a discount of 10 percent from the published price to them for single volumes.

The selling price of a volume of the Transactions is doubled when the number of that volume on hand reaches two hundred. The money derived from the sale of these copies at this double price is reserved as a fund for re-publication.

Faraday Society Transactions.

The present arrangement (May, 1921) of this Society with the Faraday Society provides for members in good standing to sub-

scribe to the Faraday Society Transactions at the special price of $2.25 per volume.

Advertisements in the Bulletin.

Members, and non-members who are applicants for admission and have deposited their entrance fee with the Secretary, may insert advertisements of situations wanted in the monthly bulletin.

Advertisements of situations open may be inserted in the monthly bulletin by members or non-members, at the discretion of the Secretary.

The Presidential Address presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 22, 1921.

OUR INVENTORY.

By Walter S. Landis.[1]

At long and irregular intervals it was the habit of the proprietor of the cross-roads general store to walk slowly through his place of business, glance to the right and to the left, and up and down, and make mental notes on the status of his stocks. So long as this crude method of determining his inventory was satisfactory to himself he remained the country store-keeper or fell by the wayside. If, through accident he developed to the stage of actually "taking stock," he abandoned the country store, moved to the nearest town and opened up a large and more elaborate, though frequently more specialized place of business.

There is a wide difference between the primitive stock taking of the cross-roads merchant and the continuous inventory, carried by our modern corporation, and we of the newer school are still theorizing as to the ways and means which keep some of the old timers in the field. At the same time when we look into our own branch of industrial activity, I think we will find its system of inventory is in much the same condition as that of the cross-roads store. Are we carrying such a form of inventory as to enable the quick determination of the quantity and quality of stocks on our shelves? Is this stock suited to our markets? Will we be able to meet our competitors on their own terms? How much do we know of the future prospects of our business? Remember I am speaking here of the industry as a whole and not of any specific branch or unit.

The industry with which we as members of this Society are associated—that one utilizing the chemical and thermic effects of the electric current—represents, on the North American continent, an invested capital of something over six hundred million dollars. As a matter of fact this may actually be upwards of a billion dollars, but our antiquated cross-roads system of keeping our in-

[1]Vice-President and Chief Technologist, American Cyanamid Co., New York City.

ventory does not permit us any great degree of precise determination of such factors. The lesser figure does not include so far as it has been possible to segregate the same, those portions of plants not exclusively a part of the electrochemical process, nor does it include generating stations where they are operated as separate corporations. The great difficulty, however, has been to determine where the line should be drawn in those industries which use the same equipment for products derived from electrochemical or electrothermic sources, and from other sources independent of the electric current. It is this indefiniteness that represents the difference between the six hundred million dollars and the billion dollars mentioned above.

The casting of a balance sheet of an industrial group the size of ours is a somewhat different task from merely keeping up the inventory of an individual unit making a part of the whole. We are dealing with factors here as fundamental items, which are usually only considered from the unit standpoint as intangibles.

My attempt at compilation will fall far short of the desired completeness we all desire but matters of this sort and in this place can always be passed on to one's successors.

LOCATION.

Our first item of consideration is the value of the location we have chosen to establish our industry. It is not unusual to hear, for example, that Norway is the logical home of the electrochemical industry, or that Germany will stifle all future competition in our line. Are we to consider on the basis of such broad and unsupported statements, that our choice of location has been an unfortunate one, that we are located on a side-street in a poor neighborhood, that America is a liability to us instead of an asset. Personally, I have no time for such propaganda. I am not even disturbed by the fact that a prominent American corporation has established a Norwegian branch factory. The mere fact that Norway seems to have an abundance of undeveloped water power will not make it the Mecca of the electrochemist, for it takes more than undeveloped water power to build up an industry such as ours, and when one considers that Norway possesses no local markets, must import every pound of coal and

coke, is short of skilled labor and uncertain as to temperament of the little unskilled labor available, I am not ready to write off very much on our choice of location.

In appraising the value of location, one must consider many factors, for example: The liberal form of government under which we live for a time showed a decided tendency towards an unfortunate socialistic attitude to industry. This now appears to have been only an incident of the war, and prospects ahead of us are that we shall soon be clear and free to develop in proper competitive and individualistic manner. Laws governing proper combinations for meeting foreign competition are becoming more constructive and helpful. Outside of England I do not believe a single European nation can today compare in as liberal prospective legislative helpfulness.

As to transportation, the war left us a great fleet of merchant ships capable of taking adequate care of our export business. Unfortunately operation of this fleet is handicapped by marine laws framed by prairie sailors. Some day our scheme of government may advance to that state of development where political expediency makes way for skill and experience in the proper planning of specialized activities. Improvement of inland navigation in many cases goes hand in hand with hydroelectric development, all of which will help to unload our railroad systems. The electrochemical industries should be the preferred customers of such inland water transportation systems because of their location.

Our railroad system is the best in the world, even in spite of the universal domestic criticism. Just ask any returning foreign traveler. But development is at a standstill, rates are impossible; in fact in this case "best in the world" means really everything is pretty poor. The railroads are in for a complete reorganization —new management, new policy, greater efficiency from fewer and better employees—and they had better start pretty soon and get it over with or industry will again be on their heels.

Recent water power legislation will surely lead to several important new hydroelectric developments and the possible establishment of new electrochemical centers. When prices of construction materials and labor drop to a point where the fixed

charges imposed on the power cost are not too burdensome, work will begin on the many long delayed projects. Our industry is bound to profit through these undertakings.

Someone has said that electricity in electrochemistry is merely an excuse for burning coal. When one looks over the fuel requirements of the heavier electrothermic industries, the statement is not a great exaggeration. Nowhere outside of the United States is there already developed, the abundance of high grade fuel that we have near our electrochemical centers. Continental fuels are of inferior grade and higher in price. Even English coals are going to be expensive in the future. Of the materials for making electrodes, we have in plenty and of such quality that today our large carbons command first place throughout the world.

It is true there are a few raw materials used in this industry and with which we are not abundantly supplied. During the war emergency special efforts were made to develop the production of these miscellaneous materials and the efforts were crowned with some success. If a fraction of the great sums of money spent on war plants which were of absolutely no use whatever toward the winning of the war—and I am not including here many plants founded upon perfectly sound engineering judgment and certain of performance but not completed, before the signing of the armistice—had been spent on the search and development of some of our less plentiful raw materials, I might have a different story to tell with respect to these less abundant materials.

I believe after due consideration of the few facts just stated that we can write our choice of location down on the asset side of our balance sheet and give it a very high value. On the other hand there is no doubt that we must place against this large asset, a small liability for shortage of a few raw materials and a larger liability for the disorganized state of our transportation systems. But so far the assets greatly exceed the liabilities, which foreign propagandists will please note.

PERSONNEL.

The chemical industry of this country is comparatively new. We did not possess the background of alchemists that Europe

had but we seem to be fast making them. Our schools of chemistry have only in the last few years taken on a semblance of Americanization, for most of our older teachers were educated abroad and equipped their laboratories almost exclusively with foreign apparatus. This has not been altogether satisfactory for our industry is primarily an American one, using American processes, worked in American apparatus, and supervised by American engineers. Aluminum, carbide, graphite, metallic sodium and a host of other products are primarily of American origin. The caustic soda and chlorine industries use almost exclusively American cells. As a matter of fact I do not know of anything in the industry of any great importance that has been brought over from Europe and held to its original European form for any length of time, and I know of only one considerable development in Europe that seems not to have been brought here at all. With these facts in mind we must agree that the American engineer is superior to the European in all electrochemical and electrothermic development, in spite of his semi-European chemical training. It is our duty to impress these facts upon the direction of our schools of higher education, and render all the assistance we can to Americanize their methods and equipment.

Our industry with six hundred million to one billion dollars of capital investment looks for a profit of from one hundred to two hundred million dollars annually to meet capital charges and provide for reasonable growth and development. This return must come from the direct efforts of those charged with the conduct of the business—the executives, superintendents, engineers, etc. In other words men largely technically trained are responsible for the earning of this enormous sum of money, and the universities and technical schools must in turn supply these men. Looking at this from a "gross" standpoint the electrochemical industries must return approximately five hundred million dollars per annum, largely *via* university products.

Only a few technical schools make direct attempts at turning out electrochemists. Some others merely provide auxiliary courses in electrochemistry, and a still larger number merely group the subject with physical chemistry. There are practically

no schools capable of properly handling post-graduate students in electrochemistry because they do not have necessary equipment.

In our schools of civil engineering we give our men regular drafting equipment. They work with standard levels and transits, and do not use small scale model testing machines in their study of materials. In our schools of mechanical engineering we provide our men with regular boiler plants and operating steam engines, not models. The students are not forced to work with miniature automobiles or internal combustion engines in any laboratories with which I am familiar. Why, therefore, should we expect in the training of our electrochemists that they should do their work in the laboratory entirely with glass beakers or similar small scale equipment? Why should the only representative electric furnace with which they ever come in contact during undergraduate days, be either a picture or a small model, or in a few particularly fortunate cases exist in some nearby industrial plant that is open to their general inspection. If we are going to really educate electrochemists, we must provide in the university as a part of the daily working equipment, not models, but actual industrial installations, and operate these before and with the student through the assistance of practical electrochemists, supplementary to the theoretical instruction and lecture work.

I very much doubt if the universities of this country have available and are spending one hundred thousand dollars per year for the direct teaching of electrochemistry. I do not know of a single school laboratory that has a thousand kilowatts available for electric furnace work, or more than a model plating or refining equipment. If the industry is going to expect the graduates of institutions operating under such handicaps to return to it a gross of some five hundred million dollars per year and a net of from one hundred to two hundred million dollars, they will have to do something for our educational institutions along electrochemical lines, otherwise the German threat may not be all propaganda.

This Society holds two meetings a year, and averages nearly a thousand pages of publications annually. Our system of keeping inventory does not permit us to determine just what net returns the industry obtains from the communications, meetings

and other services rendered by the American Electrochemical Society. It is my opinion that it adds directly a good many thousand dollars per year towards the net of the corporations. I am certain that if we include the dues of members paid by the corporations, the corporations will not have contributed twenty-five hundred dollars per year to the support of the Society, an extremely small percentage of the net return they derive from the existence of just such a body as this.

The Society is doing the best it can and to the extent of its available means to advance the interests of electrochemistry. With larger means it could do a great deal more. The officers of the Society believe that it would be unwise to attempt to raise additional funds by increase of dues. There is, therefore, only one way to obtain the greatly needed additional income which the Society could profitably use and that is through some working arrangement with industry, whereby additional funds could be secured on something other than a charity basis. Since I am merely casting up an inventory which is presumed to be a record of facts and not of opinions, I merely wish to leave this idea with my successors with the hopes that they can work something out of it.

As to the ordinary labor in our plants, I am not prepared to say that it is of as high quality as might be found in other countries, but at the same time I will not class it lower. On the other hand we use only a fraction of the quantity in this country that is used abroad. We use automatic devices much more freely. We build larger units and operate them at higher capacities. In consequence while our common labor may not be quite so steady, and is not so cheap per man hour, when we consider the quantity used I do not believe that labor places an extremely serious handicap on the development of the American industry. There are many labor abuses which will have to be corrected. The demoralization incident to the war is already being eliminated and it will probably not be long until our labor cost will not be the determining factor in foreign competition.

Reviewing our item of personnel, I think we can list the engineering ability, inventiveness and efficiency of the American engineer and the American workman as an asset of particularly

high value. I cannot place the technical school and the Society on the other side of the balance sheet, because that would put them in the false light of being liabilities, when as a matter of fact we know they are not, and have been rendering wonderful service under existing handicaps. At the same time I think we must all admit that they are not up to the standard we are desirous of setting for such institutions, and that our first endeavor in rectifying this inventory should be directed to improving the status of these two items.

I could continue in this manner to discuss many additional items, such as our research and technical organizations, periodicals, our prospective future developments, and a host of others. They all call for attention which time forbids my yielding. I am certain all will fall in with our assets.

CONCLUSIONS.

Close scrutiny of our balance sheet shows our industry to be in excellent condition. Every such report I have ever seen of a going concern always has a liability side and we are no exception. General business conditions at this time are not good. Low exchange values of foreign coins coupled with questionable economic practices in some of the European countries, are causes of temporary but immediate concern. Bad habits acquired by our legislative bodies during the war and not yet broken, will trouble us for some time. The relationship of our schools and this Society to the industry can be improved. All must be properly weighed and considered.

On the other hand the wonderful opportunities America affords for the development of our industry, the skill, activity and courage of our engineers, all against the historical background set up by Acheson, Castner, Cowles, Hall and a host of other early workers can mean only the most successful future. Let us take full advantage of the opportunity.

Lecture presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., on the evening of April 21, 1921.

RARE GASES OF THE ATMOSPHERE.[1]

By R. B. Moore.[2]

It is a curious thing that from the year 1785, when Cavendish published his classic work on the atmosphere, practically nothing was done along research lines in connection with the air until Lord Rayleigh, in 1882, got interested in the relative densities of nitrogen obtained from the atmosphere and from certain chemical compounds. He took samples of air, removed the oxygen, and accurately determined the density of the remaining nitrogen. He did the same with nitrogen from chemical compounds, such as sodium nitrate, ammonia nitrate, etc., and found that the density of the nitrogen obtained by these two methods varied. The nitrogen from the air always had one density and the nitrogen from the chemicals always had another density, the two varying by a little under one percent. For a while, Rayleigh could not account for this. He found on looking up the work of Cavendish that the latter had recorded the same difference in density over one hundred years before. Sir William Ramsay asked Lord Rayleigh's permission to take up the whole matter from the chemical standpoint, and they agreed that this should be done, and that Rayleigh, himself, should continue the work on the physical side.

Shortly after the discovery of argon, in 1894, there was a good deal of discussion among chemists all over the world as to who should have the credit for its discovery. A little over ten years ago I was in London at a dinner at University College given to Ramsay by his old students. It was the twentieth anniversary of his professorship at University College. Lord Rayleigh was the toastmaster on that occasion, and in referring to the discovery of argon he gave Ramsay the lion's share of the credit. In doing

[1] Published in abstract, by permission of the Director of the Bureau of Mines.
[2] Chief Chemist, U. S. Bureau of Mines, Washington, D. C.

this, he was generous and perhaps did not give himself full credit for his own work, but the incident showed that these two great scientists had the kindliest feeling towards each other.

In making argon, Ramsay used in the final stage of the process a mixture of magnesium powder and lime. It is advisable to have the lime well burnt and as free from carbon dioxide as possible. The air is passed through drying tubes and over caustic soda in order to remove CO_2. It then is led over heated metallic copper in order to remove the oxygen, and the nitrogen is removed by the magnesium-lime mixture, which is heated to low redness. As the nitrogen enters this tube a bright ring can be seen at the point where the gas first comes in contact with the heated mixture, and as the reaction continues this ring slowly moves down the tube. This represents a good indicator for knowing when the magnesium-lime mixture is used up. From this tube the gases are led over heated copper oxide to oxidize the CO and hydrogen formed in the above reaction, and these products are removed by caustic soda and phosphorus pentoxide. The pure argon can be collected over mercury or water, preferably the former. In this manner, Ramsay prepared eleven liters of argon, and stored it in a gas holder.

After the discovery of argon, Ramsay looked for other sources of the element, and he heard through Sir Henry Myers that Dr. F. W. Hillebrand, of the United States Geological Survey, had obtained a considerable quantity of nitrogen by heating a mineral called clevite. Ramsay suspected that this mineral might contain argon, and, therefore, wrote and asked Dr. Hillebrand to send him enough of the material to make the test. The mineral was heated and the gas obtained was sparked with oxygen, the oxides of nitrogen produced were removed by caustic soda, and after the excess of oxygen had also been removed, the gas was run into a spectrum tube. On looking at the spectrum Ramsay observed a bright yellow line which on measurement proved to coincide with the line which had been observed by Janssen, in 1868, in the chromosphere of the sun during the eclipse in that year.

On that occasion the spectroscope was first used during an eclipse, and the yellow line in question was observed in the first gaseous envelope surrounding the sun, with a depth of about 10,000 miles. The wave length of this line was determined later

by Lockyer, and shown to be different from D_1 and D_2 lines of sodium, and, therefore, it was called the D_3 line. Outside of the chromosphere is the corona which extends for two or three million miles into space. In the corona there is evidently at least one element, coronium, which has not been found up to date on our planet. It is probably lighter than hydrogen or helium owing to the fact that it exists outside of the envelope surrounding the sun, which carries hydrogen and helium.

Sir William in describing to me on one occasion what happened when he first observed this spectrum of the gas given off from clevite, stated that he was so astonished at the result obtained that he pushed the prism out of the spectroscope and wiped it with his handkerchief, in a more or less mechanical manner. He had expected to see the lines of nitrogen, or at the most, of argon, but the lines presented were quite different. A yellow line was there, to be sure, but the picture was very different. He then sent for Dr. Collie, and Dr. Travers, and others in the laboratory, and they examined the yellow line. Someone suggested that it must be due to sodium on the electrodes, so a comparison spectroscope was set up, and on comparing the sodium spectrum with the spectrum of the gas it was easily seen that the two yellow lines did not coincide. Sir William Crookes measured the wave length of the line shortly afterwards, and found that it corresponded to the yellow line which had been found by Janssen in the chromosphere.

In his presidential address, November, 1876, before the American Chemical Society, Professor J. W. Draper said: "I often look at the bright yellow ray emitted from the chromosphere of the sun by that unknown element, helium, as the astronomers have ventured to call it. It seems trembling with excitement to tell its story, and how many unseen companions it has." This is a case of scientific imagination which is worthy of record. Not many people know that Draper made this remark, and yet I think it is a case of foresight which is certainly of great interest.

The eleven liters of argon which had been prepared were shortly afterwards fractionated by Ramsay and Travers. The method of fractionation is simple.

When Ramsay and Travers liquefied their argon and drew off

the first fraction, they ran a small portion of it into a spectrum tube. The spectrum showed some extremely bright red and orange lines, as well as the yellow line of helium. The new gas was called neon. Various attempts were made to separate neon from the helium, but a complete separation was not possible until later they obtained liquefied hydrogen and used the liquid hydrogen for the separation. At the temperature of liquid hydrogen, the vapor pressure of neon is quite low, and the helium can be readily fractionated from the neon, and both gases obtained in a pure state.

Ramsay attempted to get the rare gases to react either among themselves or with other elements, but without result. The rare gases have apparently so far resisted all attempts at getting them to combine with other elements. Helium and argon were sparked with oxygen, chlorine, and hydrogen without success. Red-hot sodium hydroxide, sodium peroxide, or fused potassium nitrate had no action. Fluorine and red-hot magnesium are equally ineffective. Fisher and Schroeter have passed a discharge between the electrodes of different metals immersed in pure liquid argon, and, whereas the metals usually underwent a decided change, lithium and sodium becoming brown powders and zinc and calcium changing to black modifications, in no case could it be proven that any compound had even a momentary existence. This does not mean that the rare gases cannot be made to combine, but simply that they have not been made to combine up to date. Personally, I do not believe that they ever will, but it would be unwise to say definitely that such a result is impossible.

The thermal conductivity of helium is high. Some of the principal possible uses of helium outside of its employment in connection with balloons are in association with this high thermal conductivity. It has been suggested that this gas might take the place of oil in transformers, or of many substances where good heat conductivity is required. If any of you think, therefore, of a place where gas can be used, where it must be non-inflammable, and have a high heat conductivity, helium has a possible use.

For a while the solubility coefficient of helium, as determined, was apparently out of place. The work of Antropoff along this line was afterwards corrected by himself, and his more recent

figures (0° C., 0.00967; 10° C., 0.00991; 20° C., 0.00996; 40° C., 0.01029), place helium in its proper position in relation to the other rare gases. The solubility coefficient of a gas is the volume dissolved in one cubic centimeter of water, the gas being measured at 0° C., and 760 mm. pressure.

Onnes liquified helium in 1909. Next to hydrogen, it is the lightest liquid known. Its maximum density is at 2.2° absolute. The refractive index is 1.03; the surface tension is small, and the boiling point is 4.25° absolute. The critical temperature is 5.25° absolute, and the critical pressure is 2.26 atmospheres. The density of the liquid is 0.1459 at 2.4° absolute. Onnes used for liquefaction purposes 125 to 150 liters of helium, part of which he obtained from Dr. H. S. Miner. Thorianite is one of the best minerals from which to obtain helium, as it carries a very large percentage of helium in proportion to its weight, and it was from the thorianite which Dr. Miner, of Gloucester, furnished me that I obtained my first helium in quantity. The helium which Dr. Miner sent to Professor Onnes came from the same source.

At the present time we are installing in Washington a low temperature laboratory in which I hope to liquefy helium in reasonable quantity. If we succeed in doing this, we will be able to put at the disposal of American scientists in the laboratory the main facilities for extremely low temperature work. I trust that this opportunity will be taken advantage of, for a large amount of valuable work can be done on the properties of matter at low temperatures, particularly at temperatures between that of liquid hydrogen and liquid helium.

The compressibility of helium is 0, that is to say, helium is a perfect gas within a wide range. This is not true of some of the other gases. Neon is, if anything, more than a perfect gas, or one might call it an ultra perfect gas, because its compressibility is minus. In this respect neon is out of order with the other gases. It may be that this particular result is incorrect, but as the figure in question was obtained by the same experimenter who determined the compressibility of some of the other gases, it is probably reliable.

Another property that is interesting is the dielectric cohesion, or resistance to the passage of an electric discharge. Neon conducts

the current better than any other known gas. It is such a good conductor that if a tube containing pure neon and mercury is inverted in the dark, as the globules of mercury run down the side of the tube sufficient difference of potential will be obtained between the different droplets of mercury to cause a faint glow in the gas.

Monsieur Claude, of Paris, has used neon for special lighting purposes, the orange glow obtained from this gas being extremely beautiful, and lending itself for decorative effects. It has also been suggested that by putting the gas in a Cooper Hewitt tube, the greenish glare obtained from the mercury vapor lamp can be toned down by the orange color of the neon light.

The spectra of these rare gases are extremely interesting. The principal helium line is in the yellow. The spectrum of neon consists mainly of reds and yellows with some greens. In argon, there are numerous lines across the whole spectrum, none of them standing out prominently. There are, however, a couple of reds which are visible further towards the ultra red than the prominent lines of neon, and it is by means of these reds that we usually recognize argon visually when mixed with other rare gases.

Krypton has two very prominent lines, yellow and green, and, besides, a number of violets. This green line is one of the most persistent in the rare gases, and shows up prominently at an extremely low vacuum. It is seen in the spectrum of the aurora borealis. Xenon, meaning "blue," has a number of prominent blue lines in its spectrum. It is probably the least interesting spectrum of all.

Radium emanation, which we may consider as belonging to the rare gases, has a distinct spectrum also, in fact, just as distinct as any of the others.

Last year Dr. Nyswander, of Denver University, worked with me on some preliminary work on redetermining the spectrum of the emanation, using much larger quantities of emanation than were used by Rutherford or Ramsay. We also checked the principal lines which were found by the above observers, but did not identify a number of lines which they obtained. In addition, we found some lines which neither Rutherford and Royds or Ramsay apparently saw. We had hoped that, by letting the

emanation tubes stand and taking photographs at intervals, we might be able to get a change in the spectrum due to the formation of disintegration products. Nothing definite, however, came of this part of the work, as the volume of gas was undoubtedly too small, although we used at one time up to 1,000 millecuries. A continuation of this work will undoubtedly give results of great interest.

One of the new things started during the war was the extraction of helium from natural gas, for use in dirigibles and balloons. The need for such a gas was very early recognized by the British and French, particularly the British. Colonel F. Lucas, in charge of all the British dirigibles was over here during the war, and described to me the great advantage of a non-inflammable gas, which could take the place of hydrogen. The British were looking for possible commercial sources of helium nearly three years before we entered the war. In February, 1915, I had a letter from Sir William Ramsay stating that he was doing this, but did not have much hope of success.

In 1907, Cady and McFarland had published a report on the presence of helium in a number of natural gases, mainly from Kansas, where some of the samples tested ran as high as 1.5 percent helium by volume. Knowing this, as soon as we ourselves entered the war I suggested that helium could be obtained in commercial quantities from natural gas, and a few months afterwards the whole idea was put before the War Department by Colonel Burrell and myself. Colonel Chandler, in charge of lighter-than-air craft for the Army, at once saw the great possibility in the suggestion, and the result was that three plants were built in Texas, and we are now producing helium on a commercial scale.

The Army and Navy jointly allotted funds to the Bureau of Mines for the construction of three experimental helium plants. All of these were placed in Texas owing to the fact that the Petrolia, Texas, gas which is used by the cities of Fort Worth and Dallas was found to be rich in helium, containing 0.93 percent of the rare gas. The conditions were favorable for the operation of the plants, and two of them were placed at Fort Worth, and the other at Petrolia near the source of supply. The

plants at Fort Worth used the Linde and Claude systems respectively, and were operated under government supervision by the Linde and Air Reduction Companies, of New York. The plant at Petrolia used the Jefferies-Norton system, which had never been tried out commercially. Owing to the power necessary in connection with the Linde and Claude systems, it was felt that in order to get the costs down to a point that would be entirely satisfactory, it was necessary to try for greater efficiency. Hence, the Jefferies-Norton system, which appeared likely to give this efficiency, was installed in a plant at Petrolia, and thoroughly tried out on an experimental basis.

The composition of the Petrolia gas is usually about 31 percent nitrogen, 10 percent ethane, and heavier hydrocarbons, 57 percent methane, 0.93 percent helium, and traces of carbon dioxide and oxygen. The methane is liquefied in the lower portion of the Claude still, but the nitrogen has to be liquefied in the upper portion in order to give a reasonably high grade of helium, and the Claude plant had some difficulty in completely liquefying the nitrogen. The Linde plant had three sections to their interchanger instead of one as used by the Claude process. The final product obtained averaged 93 or 94 percent helium.

The new plant at Fort Worth, Texas, has a capacity of over five million cubic feet of gas in 24 hours, and, with a reasonable recovery of the helium, it should give when operating at full capacity from thirty to forty thousand cubic feet of 93 percent helium per day.

Plant 3, at Petrolia, uses the Jefferies-Norton process. With the higher pressure which is available in the Jefferies-Norton system in the still, and the low actual pressure of the gas coming from the compressors an efficiency is attained which is not available in the Linde and Claude systems. The work is, however, still in the experimental stage. The plant as constructed at the present time probably does not have quite enough operating leeway, and, in addition, has been subjected to a considerable amount of variation in composition of the gas as regards the hydrocarbon content supplied to it. If it could be made an operating success with as good a recovery of helium as the Linde plant has

made, it undoubtedly would produce helium at a considerably less cost.

We have found that by the use of charcoal, helium of 100 percent purity can readily be obtained. There is a selective adsorptive action on the oxygen and nitrogen, the adsorption of helium being, on the other hand, extremely small. In addition, the curve of purity holds at 100 percent up to the point at which saturation of the charcoal is reached, when the break is exceedingly sharp. Such a condition is ideal. The grade of the gas obtained just before saturation is 100 percent, and, the break being extremely sharp, the whole method is easy to handle commercially. After a run is made, if a vacuum pump is put on the charcoal, the small amount of helium which has been adsorbed can be pumped off without contamination by oxygen or nitrogen.

The origin of helium is one of the most interesting themes connected with this remarkable element. Whence does it come? Helium is in the air in the proportion of one part to 185,000 by volume. It has been assumed that the helium in the air results from radioactive changes in the earth's crust, and such an assumption is justifiable if we allow enough time for the radioactive changes to take place sufficiently. The *alpha* particle in radioactive changes is a charged helium atom, and such an explanation, therefore, for the helium in the air is at least logical. When it comes to the helium in natural gas, the situation is different. The Petrolia field, in Texas, from which we have been getting our helium is only about nine to ten miles square with a possible drainage of forty square miles, and somewhere from sixty to one hundred million cubic feet of helium has been given off from this field. Since 2,000 pounds of uranium metal in equilibrium with all its disintegration products will only give 110 cubic centimeters of helium per annum it is easy to see that it will require very large deposits of uranium ores, and very long periods of time to justify the assumption that the helium in the Petrolia gas field came from radioactive changes in the earth's crust. Not only Texas, but Oklahoma, southeastern Kansas, a portion of Illinois, Indiana, and Ohio, the northwest part of New York, and part of West Virginia, all contain large supplies of helium-bearing gas containing from 0.1 to 1.5 percent helium. It is diffi-

cult to believe that such a large area is underlain by uranium or thorium minerals in sufficient quantity to give the very large volumes of gas which are trapped below the earth's surface.

The possibility of the transmutation of other elements besides those which are commonly known as "radioactive elements" has received considerable thought and attention. The work of Ramsay and Cameron seems to give a possible explanation for the origin of helium, and also for that of neon, and perhaps the other rare gases. When a solution containing copper is placed in a quartz bulb and subjected to the action of radium emanation, they found that not only was a minute trace of helium formed, but neon was formed as well. I was in the laboratory at the time this work was going on, and watched it carefully. As regards the neon, there is no reason at all why this was not obtained as described. Ramsay was too exacting a worker to be mistaken regarding even a trace of the rare gases, and I believe that there was a very strong possibility that this part of the work was correct. A good many men who were in close touch with the work felt the same way, and only quite recently it has been suggested to me by one of these men that I try the transmutation of xenon.

If the helium in natural gas does not have a radioactive origin, it may have come from the chromosphere of the sun if we assume the commonly accepted origin of the earth.

Strutt has shown that potassium minerals at Stassfurt contain one hundred times as much helium as would be justified by their radioactive properties. The other salts associated with potassium deposits are not rich in helium. The fact that potassium is faintly radioactive taken in connection with the above observation is suggestive.

There is very little absolutely pure neon in the world, as it is necessary to use liquid hydrogen to separate it absolutely from helium, although it can be purified to a considerable extent by means of charcoal at the temperature of liquid air. This method, however, is inefficient, as only a moderate amount of neon of reasonable purity can be obtained, since most of the gas comes from the middle fractions which always contain some helium.

I also have samples of some minerals from which helium can

be obtained, particularly pitchblende and carnotite, both from Colorado. The occlusion of the gas depends to a considerable extent on the density of the mineral. The pitchblende, being more dense, occludes the helium much better than carnotite. Another sample is thorianite from Ceylon. This is rich in both thorium and uranium, and one gram will give between four and five cubic centimeters of helium. It takes a long time for the helium to accumulate. Starting with the element uranium, one-half of the element changes in five billion years, but during this period it is forming helium all the time. This rate, however, is extremely slow, for, as has been said, from 2,000 pounds of uranium element in equilibrium with its disintegration products, only 110 cubic millimeters of helium is obtained each year.

DISCUSSION.

Prof. J. W. Richards: This thought has come to me: Dr. Moore has spoken about the mysterious origin of helium. Moissan, I believe, was the first to make the suggestion that possibly the high specific gravity of the earth was due to uranium carbide. The mean specific gravity is about 5.5, which is much higher than any of the general surface rocks, and Moissan speculated that the interior of the earth was possibly uranium carbide. One consequence of that speculation is that the action of water on uranium carbide makes liquid hydro-carbons, so that gave another speculative origin for petroleum. If that speculation has any foundation, possibly the immense amount of uranium carbide in the center of the earth may be the source of the helium.

Dr. Moore: That is a possibility, Dr. Richards, and it has been brought out by Dr. Washburn in one or two of his publications. There are, however, a number of things against the explanation given. First of all, the localization of the helium. This country is the only one in the world that has helium in its natural gas in quantity, and the helium occurs along certain definite lines. For example, the probable source of helium-bearing gas starts in Texas, goes across Oklahoma, southeastern

Kansas, Ohio, into Pennsylvania, New York, and back through West Virginia and Kentucky. Helium-bearing gas does not exist in California. In the large fields of Wyoming and other places it is localized, and it is hard to believe that the center of the earth has anything to do with it. Abram Strutt found that if radioactivity of the different types of rock and soil in the earth's crust be determined correctly, and these be averaged, the figure arrived at would be too large. In other words, it would be more than enough to account for the heat dissipated by the earth. If, however, it is assumed that this average activity extends to 40 miles below the earth's surface, then it is just about enough to take care of the heat dissipation of the earth. If it is assumed that the same amount of radium exists all through the earth, and the earth is fine on the surface, there would be altogether too much radium to account for the rate of heat dissipation. This is directly opposed to the idea that the center of the earth consists of uranium carbide and metallic uranium, because wherever you have uranium you have radium.

A Member: What is the comparative lifting power of helium and hydrogen?

Dr. Moore: One hundred percent helium has 92 percent of the lifting power of pure hydrogen, although it is twice as heavy. The reason is that the lifting power is not in proportion to the relative density of the two gases, but depends on the relation of the density of each gas to that of air. For example, the density of air is 14.42, helium is 2, and hydrogen 1. Subtract 2 from 14.42 and you get 12.42; subtract 1 from 14.42 and you get 13.42; so that the relative lifting power is as 12.42 is to 13.42, or approximately 92 percent.

A Member: I would like to ask a question as to the relative cost of hydrogen and helium by the latest system devised.

Dr. Moore: The new large production plant is producing helium at about six cents per cubic foot. Before the war, if you wished to buy a cubic foot of helium it would cost about $1,700 to $2,000, so you can see that fair progress has been achieved. Plant No. 3, using the Jefferies-Norton process, if it is a real success, should cut the figure of six cents in half,

so that on this basis helium might cost from $25 to $30 for a thousand cubic feet. Hydrogen can be manufactured cheaply, probably for $5 to $6 a thousand cubic feet, under certain conditions of operation, particularly where the plant is running continuously. On the other hand, this price is not a fair one, and is not actually achieved under normal conditions, as the plants are not run continuously, and are more likely to be run periodically. This makes the actual cost of hydrogen considerably higher than the figure I have given.

In estimating the relative cost of the use of helium and hydrogen in airships, the item of fire hazard must not be lost sight of. The extra expense of the helium may be largely written off against insurance from loss of life and millions tied up in the craft.

A Member: Have not dirigibles actually been operated filled with helium?

Dr. Moore: No. There is a good deal of work to be done before building a dirigible which is well adapted to the use of helium. It is necessary to conserve the gas, owing to its additional cost, and it should not be handled in the same way that hydrogen is handled at the present time. For example, "valving" should be reduced to a minimum. One way to do this is to keep the weight carried by the ship as constant as possible. When you are using gasoline motors, gasoline is being consumed and the weight carried by the ship is, therefore, gradually decreased, and there is a tendency to rise. By condensing the water from the exhaust of the engines, the weight of the water obtained is about equal to the weight of the gasoline used. There are other things of the same kind that the Army and Navy are working out, and it will probably be a year, I think, or perhaps two years, before there is any chance of using a large dirigible filled with helium. It is coming, however.

A Member: You mean the water of combustion is condensed?

Dr. Moore: Yes; the vapor in the exhaust of the engines. I think the weight of the condensed water has a ratio to the weight of the gasoline of about 103 to 100.

Dr. E. F. Northrup: Assuming that the earth is a sphere cooling at a certain rate, having a certain thermal conductivity, the recent discoveries of radio-active material in the earth have, as I understand it, entirely upset the value of all those speculations as to the age of the earth?

Dr. Moore: Yes, and it has been a good thing, because it has brought the physicists closer to the geologists. For a long while these two groups of scientists were at loggerheads over the age of the earth. The first claimed that, on the basis indicated by the loss of heat from the earth, its age could not be more than twenty million years. The geologists said that this length of time was altogether too small, and that they required several hundred million. Our knowledge of radioactivity has brought the two groups of men much more closely together. For example, if the radium in the earth's crust takes care of the loss of heat largely, it means that the earth is cooling much more slowly than Kelvin figures it, and, therefore, it brings the correct figure much more closely to what the geologists have claimed.

Starting with any given amount of uranium element in an ore, it would take about five billion years for half of the uranium to change. On the other hand, it only takes about ten million years for a uranium mineral to come to equilibrium with all its disintegration products. Pitchblende is what we call a primary or old mineral, and all the disintegration products are in equilibrium. This would indicate that such a mineral is at least ten million years old. Some scientific men, particularly Strutt, have tried to indicate the age of uranium and thorium minerals by calculating the rate at which helium is formed in them. They have obtained a rough approximation, but the trouble is that different minerals have different densities and the helium diffuses from the mineral at different rates. Some minerals hold helium exceedingly well, such as thorianite, but in all cases there is some diffusion.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

INTRODUCTION TO SYMPOSIUM ON CORROSION OF IRON AND STEEL.[1]

By W. H. Walker.[2]

The corrosion of iron and the rotting of wood are two sources of great economic loss which have many factors in parallel. The latter has been shown to be due to micro-organic growth, and upon this knowledge has been predicated methods for arresting or entirely preventing this loss. But notwithstanding this knowledge many structures of wood are allowed to decay with little or no attempt towards their preservation. The fact that more wood can be had to replace that destroyed is obviously considered a justification for allowing this wastage to continue. The same is true of iron. The fact that iron suffers from what is known as "rust" has been common knowledge for centuries; the cause of this action, and many of the factors which control its rate have been understood for some twenty years; and yet we daily see railroad bridges eaten with rust, freight cars covered with great red barnacles, hot water pipe systems breaking down, and wire fencing in tatters—all because more iron and steel can be obtained to replace that so destroyed. The fact that the cost of replacement is frequently far in excess of the cost of the material itself greatly multiplies this economic loss and makes the situation less excusable.

The mechanism of corrosion is now fairly well understood. Whitney in 1900 showed it to be an electrochemical phenomenon, obeying the laws of electrochemistry. It was the privilege of the writer to demonstrate in 1907 the function of oxygen in corrosion, and to apply the experimental facts to the preservation of many engineering structures. The engineering public, however, has

[1] Manuscript received January 26, 1921.

[2] Professor of Chemical Engineering, Mass. Inst. of Tech.

been slow in availing itself of the published work on corrosion probably for a number of reasons. First, the entire literature of corrosion is full of apparent contradictions and obvious misstatements. This is occasioned by the fact that corrosion is a most complex phenomenon and that factors which may be controlling in the results are frequently entirely overlooked. No two men have the same sample of iron and steel; the heat treatment is generally different, the analysis imperfectly known; the state of the surface and the finish is neglected, and a host of other important conditions completely ignored. No wonder the results present discrepancies, and the public fails to show an interest in them. Second, certain conclusions which in the early days seemed to logically follow from the electrochemical theory of corrosion have been shown to be erroneous, and have led to disappointing results. Possibly the logic was false; but at any rate we cannot crown the theory with any far-reaching beneficial results. If I may paraphrase, "the evil that a theory does lives after it; the good is oft interred with its bones" The theory that the earth was flat delayed the discovery of America by a number of centuries; the phlogiston theory guided experimenters to fruitless fields of investigation and wasted much valuable time and energy. And so with the doctrine that homogeneity of structure in iron and steel, insures an absence of corrosion. The public is still told through advertising propaganda that the old Newburyport bridge withstood Atlantic Ocean storms for over one hundred years because the iron with which it was built was pure and homogeneous, when, as a matter of fact, the majority of the links of the great chains were very impure and extremely heterogeneous. The further fact that when these very pure links were rolled down to sheet form and exposed to the weather, they rusted like modern iron and disappeared in a few years, is conveniently ignored. The old blacksmith's forge apparently introduced an element of protection which has not yet been predicted by the electrochemical theory nor realized by laboratory experimentation.

Corrosion may be divided into two classes—that taking place in the atmosphere with free access of the oxygen of the air, and that in positions from which the air is or can be excluded. In

the first field, the work of Mr. D. M. Buck stands pre-eminently the greatest contribution made in the art of preventing corrosion since the introduction of hot galvanizing. Impartial evidence is now legion that no commercial iron or steel so well withstands atmospheric corrosion as does steel containing approximately 0.2 percent copper. When thus alloyed even the much maligned Bessemer steel excels in resistance to corrosion the widely heralded pure open-hearth iron. Unfortunately, copper-bearing steel is not a child of the electrolytic theory, although we have no doubt that when adequate explanation of the wonderful effect of this small amount of copper is finally suggested, it will be found to be essentially electrochemical. With the unbroken record of successful achievement now possessed by copper-bearing steel, and the low cost of metallic copper, there seems to be no excuse for the fabrication of those structures which must withstand exposure to the weather, from any other material.

But a copper-bearing steel produces its own protective covering only when the oxygen concentration is high. When the amount of oxygen is limited, as when the structure is immersed in water, other protective means must be found. If all of the oxygen in a system could be removed, corrosion would cease. This fact was early recognized by Mr. F. N. Speller, and the careful experimentation carried on by him during the last twelve years in the application of this principle to the preservation of engineering structures, is now being crowned with success. Enough operating data from large installations are now available to demonstrate the effectiveness of this method of conserving iron and steel.

The work of Henry A. Gardner has done much to improve the protective quality of paint, while protective coatings of zinc, aluminum and tin have each received much attention. It is interesting to note also that the protection of iron structures such as a steam boiler or a condenser, by making the structure cathodic by continually passing through it a small direct current, has taken commercial form in what is called the Cumberland process, and has apparently found a place in marine engineering. While rusting iron is still an all too common sight, yet real progress is being made, and the future for anti-corrosion is bright.

DISCUSSION.

J. A. Aupperle[1]: In Dr. Walker's "Introduction to Symposium on Corrosion of Iron and Steel," he has called attention to the fact that "corrosion is a most complex phenomenon and that factors which may be controlling in the results are frequently entirely overlooked." We agree with Dr. Walker in this statement, as we know that, based on atmospheric tests of bare, uncoated sheets, that copper bearing steel is being exploited for many different purposes for which it is unsuited.

Dr. Walker refers to the discrepancies in corrosion tests, and refers to conclusions which in the early days seemed to logically follow from the electrochemical theory of corrosion, and that these conclusions have been shown to be erroneous.

It seems that Dr. Walker has lost faith in the electrochemical theory as relates to corrosion problems. This is probably due to the results which were obtained in atmospheric tests on bare, uncoated sheets.

While it is a fact that in sulphuric acid of definite concentrations and also in atmospheric tests of bare sheets, copper has slowed down the rate of corrosion, the reason has not yet been made clear. It may be, however, that copper under these conditions acts in a manner to exclude the electrolyte, whereas under other conditions copper accelerates the rate of corrosion, as is shown in a paper which was recently presented before the Society.[2]

Dr. Walker refers to the sheets made from these Newburyport links rusting like modern iron and the information being conveniently ignored. We conducted tests on a 26-gauge sheet made from the Newburyport links, which analyzed as follows:

Si	*S*	*P*	*C*	*Mn*	*Cu*	*O*	*N*
0.042	0.014	0.023	0.120	0 008	trace	0.068	0.003

After the usual mill treatment for this class of material, this 26-gauge sheet was corrugated and placed on a rack at an angle of 30 degrees at Middletown. This sheet has been exposed to the atmosphere from July 11, 1913, until the present time. In this very same test we have had failures of low copper Bessemer steel

[1] Chief Chemist, American Rolling Mill Co., Middletown, Ohio.

[2] Observations on the Corrosion of Iron and Steel. By J. A. Aupperle and D. M. Strickland. Trans. Am. Electrochem. Soc. 1921, 39, 123.

in from 13 to 69 months. We have also had failures of four different brands of copper bearing steel in from 76 to 90 months. These results should satisfy Dr. Walker that we have not endeavored to ignore the results we have obtained by rolling sheets from the Newburyport links, but that the test had not gone far enough to show the failure of the sheet made from the iron links.

A. S. CUSHMAN[3]: It is, of course, perfectly natural that Dr. Walker should have become a strong proponent of the copper alloy theory in corrosion resistance, and it is noteworthy that he now deserts the so-called electrolytic theory of corrosion and seems to point out that homogeneity of structure of iron and steel is not worth while, from a corrosion standpoint. My own recollection is, and I think the record will show, that Dr. Whitney neither formulated a theory nor attempted to prove anything. He published, as I recollect it, a short paper, in which he suggested, as the result of a passing observation, that the corrosion of iron might be explained or linked up to the Arrhenius, Van't Hoff, and Nernst conceptions of the theory of solutions. Dr. Whitney stated that this suggestion might be sustained by careful research which he thought worth while. He did not, however, preempt the field, but put his suggestion out as an invitation to men who had more time to enter this field of investigation. Dr. Walker has cited a number of authorities who sustain his views on copper bearing steel, but he chooses to ignore by citation any workers in the field who disagree with his opinions. Dr. Walker states that in 1907 he had the privilege of demonstrating the function of oxygen in connection with corrosion. I may state that in 1905 and 1906 I had already demonstrated, by the use of phenolphthalein the formation of electro-positive and negative nodes whenever iron or steel is rusting. This led to the development of the ferroxyl test which proves electrolytic action. Now a thing that is proved is not a theory. The electrolytic explanation of corrosion is not to be evaded or avoided, no matter whether it coincides with an individual bias or prejudice or not.

D. M. BUCK[4]: I am rather surprised at Mr. Aupperle's statement that the Newburyport bridge links showed a pure ferrite

[3] The Institute of Industrial Research, Washington, D. C.

[4] Metallurgical Engineer, American Sheet and Tin Plate Co., Pittsburgh, Pa.

structure. I have in my possession some thirty or forty photomicrographs showing a number of different links of this old bridge, and only two or three of these photomicrographs indicate pure ferrite structure. All of the rest show a very heterogeneous structure, the carbon in some instances running as high as the eutectoid (about 0.85 carbon).

Referring to Mr. Aupperle's criticism of Dr. Walker's statement regarding the corrosion of sheets rolled from these old links, I have no doubt that Dr. Walker based his reference on Dr. Cushman's own statement in Bulletin No. 5, The Institute of Industrial Research, in which Dr. Cushman shows that these links were fortunately heavy enough to be used as sheet bars and that on rolling them down into 16-gauge sheets and exposing them to the weather, they corroded the same as modern material.

Colin G. Fink[5]: Although the original composition of the links is the same, the final composition, the distribution of carbon and physical structure of the sheets may be entirely different, and consequently the corrosion rate entirely different.

H. E. Yerbury[6] (*Communicated*): The electrolytic theory serves very well as a general explanation of corrosion data which have come to my notice in the study of ferrous metals, yet there are several anomalies which require further study; for a great difference necessarily exists between the behavior under the same conditions of pure metals and those used in general engineering work.

The skin of a rolled metal and the chilled surface of a casting are more resistant than the interior, and when one realizes that there are upwards of twenty elements added in steel making it is obvious that corrodibility must vary with its composition. A vast field of experimental research is still open to metallurgists.

Research work should, I think, be extended to include the production of a natural high resistant skin and the application of an artificial coating on metals subjected to corrosive action.

W. H. Walker (*Communicated*): It is obvious from a reading of my paper that not only have I not abandoned the electrolytic theory of corrosion, but that I predict that when the explanation

[5] Consulting Electrometallurgist, South Yonkers, N. Y.
[6] Electric Supply Dept., Sheffield, England.

for the remarkable behavior of small amounts of copper in reducing corrosion is explained it will be found to be essentially electrochemical. Certain conclusions which at first seemed to follow from the electrolytic nature of corrosion have now proven themselves erroneous. Mr. Aupperle is correct in surmising that the very complete and careful corrosion tests of the American Society for Testing Materials on uncoated sheets has strengthened me in this conclusion. In these tests it was shown that notwithstanding the homogeneity of the pure open-hearth irons, sheets made from these materials failed long before sheets of corresponding thickness made from steel containing ¼ of 1 percent copper.

Dr. Cushman chides me for not mentioning specifically those tests in which the pure irons have withstood corrosion better than the copper steels. Such instances are like the snakes of Ireland—there aren't any.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

THE GAP BETWEEN THEORY AND PRACTICE IN THE PRODUCTION OF CORROSION-RESISTING IRON AND STEEL.[1]

By William D. Richardson.[2]

Abstract.

A general discussion of the explanation or theory of corrosion-resisting iron and steel and their alloys. Practical results have been empirically attained, and at present theory is very much lacking. Lack of fundamental data of the primary action of oxygen on metals and alloys is also hindering progress. The electrolytic theory of corrosion is discussed at length; also the influence of oxygen, in detail, and the role of adhering rust. Accelerated corrosion tests are studied, and their defects pointed out. The behavior of copper-bearing iron, silicon-containing cast-iron, nickel- and nickel-chromium steels, nickel-copper steels, chromium steels, and nickel-cobalt-chromium alloys is discussed.—

[J. W. R.]

GENERAL CONSIDERATIONS.

Our knowledge of the phenomena of corrosion may be compared to the general state of learning concerning the laws of chemistry when in the course of the historical development of that science some insight had been obtained into general chemical laws and theory, and a great mass of practical, technical and workshop information had accumulated, but when at the same time an intimate connection between theoretical chemistry and the practical arts of chemistry had not been worked out. This was the state of chemistry during the latter half of the eighteenth

[1] Manuscript received March 2, 1921.

[2] Chemical Engineer, Swift & Co., Chicago, Ill.

N. B. In editing this paper to conform with the rules of the Society, metals acting as anodes in a voltaic couple are given the — sign.

century. One might go further and say that this method of development is not peculiar either to chemistry or corrosion but has been the rule of development of all sciences and arts. The practical arts born of necessity develop first. Theory (preceded in the misty beginnings by vague speculation) has its inception much later, and at first following a parallel course of development with practice, finally converges on the latter, whereupon the two proceed together hand in hand. This convergence of theory and practice in connection with the corrosion of metals has not yet occurred.

Investigations of the processes of corrosion, particularly as affecting the varieties of iron, have proceeded so far that they have yielded a moderate crop of information and a fairly good working theory, but not so far that the results are capable of application in important practical ways. The studies so far made have not taught us how to modify the composition of iron and steel so as to produce a finished metal with considerable resistance to corrosion without seriously modifying desirable and essential physical properties. An immense literature has meanwhile accumulated on the subject, and unfortunately much of this literature has the indefiniteness characteristic of writers groping in the dark about a subject whose outlines are still vague and indefinite.

Indeed, the facts necessary for the foundation of a complete theory are by no means established. Many investigations are necessary in the fields of passivity, the relation of the different metals to oxygen and hydrogen, the anomalies of the electrochemical series, and the mutual relations of metals and non-metals in alloys, before the necessary data will be available.

EMPIRICAL RESULTS.

On the other hand, working without reference to theory, metallurgists have produced some alloys of iron (and of other metals also) which are for practical purposes non-corrodible and at the same time possess high tensile strength and hardness, and others which are corrosion-resisting to a greater or less degree. These empirically developed alloys make use for the most part of nickel, cobalt, chromium, copper and silicon for conferring resistance to corrosion on the ferrous composition. In order to

make the list complete it is necessary to mention also graphitic carbon, which, incorporated in cast iron, has been used unconsciously since the middle ages for the production of a corrosion-resisting alloy. Some of the metals named have also been used for the production of steel substitutes, that is, non-corrodible alloys, with some of the properties of steel but containing no iron as an essential ingredient.

Although the fundamental theory of corrosion is fairly well developed and although several non-corrodible alloys have been produced without reference to theory, the gap between theory and practice at the present time is vast and profound. There is no theoretical connection between the non-corrodible alloys and the general theory of corrosion, nor has the latter been productive as yet of important practical results. Perhaps the most ambitious attempt to produce a non-corrodible metal, building on theoretical grounds, was that which resulted in the production of nearly pure iron by the open hearth process, but the theoretical basis in this case was insufficient.

LACK OF DATA.

If I were asked to name the most important study in the further development of the theory of corrosion, I would answer unhesitatingly, the study of the influence of oxygen and oxidizing agents on metallic surfaces. Before we can proceed from theory to practice in the production of non-corrodible or little corrodible alloys, our theoretical knowledge of the influence and effect of oxygen on all the more important metals and alloys must be carefully worked out. Our knowledge of this influence and the resultant phenomena are quite inadequate. The precise nature of the passive condition of metals remains a mystery and the relation, if any, between the passive condition as induced by powerful oxidizing agents, such as chromic and nitric acid, and the condition of the surface of such a metal as aluminum under ordinary conditions when exposed to the air, remains to be worked out. In the relation of the metallic surface to oxygen or in what I have termed the oxygen influence on metals, we are warranted in thinking lie buried many of the secrets relating to corrosion.

The second most important study in connection with corrosion is that relating to the anomalous behavior of many metals com-

pared to what might be expected according to their position in the electrochemical series. According to the solution tension theory of Nernst as applied to corrosion phenomena by Whitney, Walker, Cushman and others, the solution tension of a metal should have a rather direct relationship to the rate of corrosion. The effect of solution tension is, however, easily overbalanced by other influences, in particular the influence of oxygen, so that many metals do not corrode in proportion to their solution pressure. Naturally, the investigation of the anomalies of the electrochemical series is closely connected with that of the influence of oxygen on metallic surfaces.

THE ELECTROLYTIC THEORY OF CORROSION.

Any review of the present state of the theory should begin with the establishment of the electrolytic theory following the long and heated controversy between the advocates of this theory and the so-called acid theory of corrosion. At present we may regard the electrolytic theory as established; and at the same time we may regard the acid theory of corrosion as established as well, since it is quite certain that corrosion will not proceed in the absence of hydrogen ions or their equivalent. Carbonic acid, however, can hardly be considered to play the important role once credited to it, for corrosion of iron proceeds at a notable rate in the presence of water and oxygen alone. Oxygen is of the utmost importance in promoting the continuance of corrosion by acting as a depolarizing agent, and this action is particularly prominent in the corrosion of iron and its alloys. If, however, the hydrogen active in corrosion is liberated at corrosion cathodes with low over-voltage, polarization supervenes less readily and corrosion proceeds at a greater velocity than in the case of a comparatively pure metal containing no suitable corrosion cathodes in its composition. Oxygen is more necessary to, and causes greater acceleration of, corrosion in pure iron than in an impure alloy such as cast iron, for in the absence of much oxygen relatively pure iron corrodes at an extremely low rate, but in the presence of oxygen at a comparatively rapid rate.[3]

The opposite behavior of relatively pure iron when compared

[3] Experiments on the Corrosion of Iron. William D. Richardson, Proc. Am. Inst. Chem. Eng., 1920, 13, Part 1, 277.

with cast iron under different conditions of corrosion is one of the most striking phenomena connected with the subject, and when correctly interpreted will probably afford illuminating data.[4]

This behavior manifests itself when the comparison is made in the presence and absence of oxygen, and the ordinary water-atmospheric type of corrosion is allowed to proceed under various manipulations. The differences are again manifest when the two types of metals are subjected to the action of non-oxidizing acids such as sulphuric and hydrochloric and an oxidizing acid such as nitric. The purer metals dissolve at a much lower rate than cast iron in the non-oxidizing acids, but at a much higher rate in the oxidizing. Under the influence of various catalysts the behavior is again opposite.[5]

The significance of this opposite behavior of relatively pure iron and mild steel when contrasted with that of relatively impure cast iron lies in the interest which it has for both the theory of corrosion and the production of corrosion resisting alloys. It is apparent from this behavior of pure and impure iron that it is possible by the addition of small quantities of impurities to iron to induce a different and indeed opposite reaction when the alloy is brought under certain corroding influences, and the purpose of the experimenter naturally would be, knowing the general fact, to add those materials which in the smallest proportion would produce the effect without seriously modifying the working properties of the metal. Thus far, in practice, only copper, as noted below, has been made to fulfill these conditions economically.

Mallet, as early as 1838[6] called attention to the fact that alloys of iron with potassium, sodium, barium, aluminum, manganese, silver, platinum, antimony and arsenic corroded more rapidly than unalloyed iron, and that alloys with nickel, cobalt, tin, copper, mercury and chromium (in order of increased effect) corroded less. Precise and complete studies of these alloys, with varying proportions of the alloying metal, in relation to corrodibility, are still wanting; nor has the theory covering the matter been devel-

[4] Experiments on the Corrosion of Iron and Steel—Rates of Solution of Iron and Steel in Non-Oxidizing and Oxidizing Acids, Proc. Am. Inst. Chem. Eng., 1920, **13**, Part 1, 169 and 265. The Solution of Metals in Acids as Related to Corrosion, Trans. Am. Electrochem. Soc. (1920), 38, 245.

[5] The Solution of Metals in Acids as Related to Corrosion. Trans. Am. Electrochem. Soc. (1920), 38, 245.

[6] British Ass'n Rep. (1838), 166.

oped. Indeed, we are somewhat if not equally at a loss with respect to the corrosion-resisting properties of grey cast iron, and cannot say positively to what substance or substances it owes its resistance; or if we ascribe it to graphitic carbon we cannot say why.

The effort to produce a corrosion-resisting metal by making commercially pure iron has not been highly successful. From theoretical considerations it seems doubtful that any quest in this direction will ever be successful since the purest electrolytic iron obtainable has been found to be highly corrodible in the presence of air or oxygen. This failure or partial failure may be attributed to the neglect to take into consideration all the active factors of the electrolytic theory. Thus, while emphasis was laid on the influence of impurities (presumably acting as cathodes) in accelerating corrosion, and hence the lessened corrosion consequent on their elimination, cognizance was not taken of the fact that these conclusions applied only in the absence of oxygen, and that under atmospheric corrosion the oxygen influence was dominant and determining. At best, and in the absence of oxygen, the adverse influence of the common minor impurities may have been overemphasized. Pure iron as corrosion-resisting metal is the result of incomplete or imperfectly applied theory.

Nor would a review of the development of the theory of corrosion be complete without mention of the intense and ofttimes bitter argument over the comparative values of "iron" and "steel" as corrosion-resisting metals. This discussion, while not based on theoretical grounds, occurred during the years when the electrolytic theory was developing, but before any theory was certain of final acceptance.

THE RELATIVE CORRODIBILITY OF IRON AND STEEL.

From about the year 1875 to the year 1910, metallurgists, chemists, manufacturers and users of steel were actively engaged in the controversy concerning the relative merits of wrought or puddled iron compared with steel made by the newer Bessemer and open-hearth processes, for resisting corrosion. This discussion commenced long before Arrhenius had announced the ionic theory (1897) or Nernst had explained galvanic action by electrolytic solution pressure, and it cannot be certain that it is yet

ended, although on the basis of the numerous published experiments it should have been laid in its grave long ago. The controversy lasted longer than it otherwise would have done, in all probability, if it had been merely a scientific question, but since commercialism played a considerable part in it, it was unduly prolonged. Experimenters were numerous and elaborate series of tests were carried out, some of the most important being by William Parker prior to 1881, by Rudeloff prior to 1902, and by Howe and Stoughton prior to 1908. These experiments bear directly on the problem; but Farquharson (1882), Andrews (1884) and Diegel (1903) made experiments on polarity which although of a negative character were important for the general problem. Summing up the polarity experiments, it may be said that composition does not determine polarity, and that during the course of any given polarity experiments there may be numerous reversals. This indicates that another factor besides composition of the metal in these cases determines the direction of the corrosion current, and it may not be amiss to say at this point that this factor is undoubtedly oxygen and the oxygen products of corrosion. The general results of all the experiments on iron *versus* steel of approximately similar composition sometimes showed greater corrodibility in one case and sometimes greater in the other, Here, too, it must be evident to the impartial reviewer that some factor outside of composition determined the course taken by corrosion in the individual cases, and again this outside factor was evidently oxygen and the oxygen products of corrosion. This discussion of the relative merits of iron *versus* steel served to sidetrack the main issue for a considerable time, but now that it may be considered to be out of the way, the investigator of the present time is free to go forward without prejudice. The old controversy in its crude form should be relegated to the limbo of lost causes or drawn battles.[7]

THE INFLUENCE OF OXYGEN ON CORROSION.

The rates of corrosion in water in the presence of air or oxygen, of common Bessemer and open-hearth steel as well as their more aristocratic and highly-recommended substitutes, lie

[7] For review of the controversy concerning the relative merits of iron and steel, see J. Newton Friend, The Relative Corrodibilities of Iron and Steel, Trans. Faraday Soc., XI, 204.

very close together. What they may be in water in the absence of oxygen is not at present subject to investigation, for no satisfactory method has been developed for the purpose. The amounts entering solution under these conditions are small within ordinary periods of time in consequence of an extremely low rate of solution. Such results as have been obtained are again of the same order.

Since the rates do lie close together, in different experiments, especially in the hands of different investigators, oftentimes one or another kind of metal will show to advantage and, again, to a disadvantage, just as when different plates of the same variety of iron are under investigation. The important point is that under like conditions the losses and the differences between losses are of the same order of magnitude, indicating no very radical difference in behavior.

When corrosion takes place under the influence of oxygen, the action of the latter is so intense as to overbalance the different effects of the common minor impurities in the metal, which otherwise might act in such a way as to increase or decrease the relative rates. Thus we are not warranted in believing that slight differences in the amounts of the ordinary impurities present can prove to be an important factor in increasing or decreasing the rate of corrosion in the presence of the immensely overbalancing influence of oxygen. If, however, for reasons which we do not yet understand, any metal, while under corroding influences, developes a tightly adherent, uniform coating of rust, this may serve to protect against further corrosion in the same manner as a protective coating artificially applied. These facts lie at the base of much of the superstructure of contradictory and questionable evidence and opinions in the literature.

It would seem as though some investigators had not fully realized the comparative magnitude of the various factors influencing corrosion. It seems necessary to repeat and emphasize the dominating and determining influence of oxygen over the ordinary variations in composition of iron and mild steel; so that in the presence of air the effect of these variations is practically negligible on the rate of corrosion. Thus in order to measure the relative merit of different metals it becomes necessary to determine their life in service rather than to determine the rates of

corrosion in order that minute differences in rate may be sufficiently magnified into a measurable time factor. Whatever the rate of corrosion would be if influenced only by the composition of the metal and the external circumstances of corrosion, this rate seldom is permitted to go forward without serious modification due to the action of the products of corrosion. In the first place hydrogen released by the corrosion currents may be absorbed, if the sample in question is comparatively pure iron, and this absorption tends to bring about polarization currents and halt the action, but in the case of less pure samples containing in their composition corrosion cathodes at which hydrogen may be released with comparatively low over-voltage, corrosion or solution in acids may go forward more continuously. More serious interference with the fundamental rate is occasioned by the behavior of the oxidized products of corrosion or rust. It is true that when the sample is submerged continuously, as in fresh water or sea water, the unmodified rate (taking into consideration the hydrogen influence) is approximately maintained, provided the surfaces remain clean and free of rust.

THE INFLUENCE OF RUST.

But it is in the atmospheric type of corrosion that the products exert their greatest effect and produce the most anomalous changes. We may distinguish three principal physical conditions of the rust:

1. The rust is rather uniformly distributed over the surface of the metal, adherent locally but loose.
2. The rust is irregular, but tightly adherent in patches.
3. The rust is uniformly and tightly adherent over the entire surface.

Under condition 1, corrosion is accelerated rather uniformly over the entire surface; condition 2 tends to produce pitting and early failure, but in condition 3 the rust acts as a protective coating, delaying the normal process of corrosion and protecting the metal for a very considerable period. Although the fundamental rate of corrosion might be nearly the same in the three rust-producing types indicated, and independent of the "rust effect," the actual life of the plates when exposed to the atmosphere would vary greatly. Unfortunately our knowledge of the

causes which bring about close rust adhesion is entirely inadequate. It appears to be true that rust adheres tightly in the case of cast iron and in the case of copper-bearing iron, and this may be due to reversal of polarity in the sense that in one case the carbon and in the other the copper becomes anodic, but definite proof is wanting.[8]

In this discussion I have not mentioned the influence of mill scale, but it is well known that mill scale acts in the same manner as rust, but more intensely, causing, when irregularly adherent, deep pitting, and when uniformly adherent, protection of the metal. It is obvious that the "rust effect" is of far greater importance than the composition of the metal in determining the life of a sheet undergoing atmospheric corrosion, although in some unknown way composition in part determines the course of the "rust effect." Under different conditions of corrosion, however, products of corrosion may behave differently so that conclusions drawn from one set of circumstances are not certainly applicable under another.

SPECIAL TYPES OF CORROSION.

In the foregoing theoretical discussion I have laid special emphasis on the influence of oxygen, since this influence is the outstanding, characteristic and powerful influence in the ordinary types of corrosion. It is necessary to mention, however, several influences which come into play, especially in atmospheric corrosion, in large cities and industrial centers where acid substances and sulphur compounds are continuously escaping into the air. In particular, in the presence of hydrogen sulphide, corrosion follows a somewhat different course than in the presence of pure air and moisture. Copper and brass are affected to a far greater extent in the presence of hydrogen sulphide than in its absence. On iron and steel the effects have not been worked out, but the relative acceleration is less than in the case of copper and some other metals. In the case of iron the sulphide formed is soon oxidized to basic sulphate, which thereafter acts the role of rust. When an atmosphere is laden with acid fumes of different sorts, corrosion will undoubtedly follow a different course than in the presence of air and moisture alone. Specific studies of the

[8] Experiments on the Corrosion of Iron and Steel, Proc. Am. Inst. Chem. Eng., 1920.

effects of different concentrations of different acids in conjunction with atmospheric corrosion are wanting.

ACCELERATED CORROSION TESTS: CORROSION FACTOR.

All investigators of corrosion phenomena have desired and sought for a so-called corrosion factor which when applied to a given sample of iron and steel would indicate its relative corrodibility compared to a standard sample. Although it has been shown many times over that the rate of corrosion varies with the circumstances of corrosion, chemists have persisted in attempting to apply a single corrosive medium which should supply the factor. For this purpose sulphuric acid of different strengths (usually 10, 20 or 50 percent) has been applied more than others, and although the results have not proven comparable to those obtained under various conditions of service, the method is still applied. For example, Sir Robert Hadfield[9] has reported that chromium steel "does not show satisfactory corrosive resistance in 10 percent sulphuric acid solution. The alloy steel containing 10 percent shows a loss of 18 percent, and that with 15 percent chromium a loss of no less than 33 percent." Such steel showed better resistance to 50 percent sulphuric acid, and was decidedly resistant under atmospheric corrosion. Based on sulphuric acid tests, commercially pure iron shows a very low corrodibility, and it might be argued from this that iron would corrode in somewhat inverse proportion to its purity. This is so far from the truth, if we consider only natural corrosion in which oxygen, water and carbon dioxide are concerned, that the opposite is the more exact statement of the case—the more impure the iron the less does it tend to corrode; witness grey cast iron with its high graphitic carbon and silicon content.

Although it is true that in dilute non-oxidizing acids pure iron dissolves with extreme slowness, how far this is due to the inherent tendency of such iron to dissolve, considering, of course, all of the composition factors involved, and how far it may be due to quite another property, namely, the ability of the metal to absorb hydrogen and become polarized, is a debatable question difficult of proof. On the other hand, in the presence of oxygen this behavior of pure iron is quite different, since it corrodes

[9] Corrosion of Alloy Steels, Trans Faraday Soc., XI, 187.

very much faster than impure forms of iron, such as grey cast iron, white cast iron, malleable iron, etc., and at a rate not very different from that of mild steel. The opposite behavior of the purer kinds of iron under oxidizing and non-oxidizing conditions (as discussed before in this paper) suggests the necessity of two corrosion factors. Such double factors have been suggested,[10] but require much more work before their general utility can be established. However, the general principle of a double factor appears to be worthy of study and elaboration, one factor being developed under non-oxidizing conditions and the other under oxidizing.

Sulphuric acid appears to have some special properties which recommend it in corrosion tests, although up to the present time it has not proved itself to be the long-sought medium. While it is in the ordinary sense non-oxidizing, it is capable of exerting the oxygen influence on the metals more sensitive to oxygen influence, such as aluminum, even at low concentrations. At higher concentrations and especially under the influence of heat, its oxidizing tendency is more marked. Thus in corrosion tests it lies somewhat between a strictly non-oxidizing acid and an oxidizing one such as nitric. So far, theory favors its use, but it is extremely doubtful that any single index arrived at with sulphuric or other acid will prove satisfactory.

COPPER-BEARING IRON.

Of the entire list of ordinary and special, open and proprietary varieties of iron and mild-steel which have been advertised as possessing corrosion-resisting properties, copper-bearing iron appears to have some special and peculiar properties which seem to warrant special consideration. The manufacture of iron or mild-steel containing a small quantity of copper, for the purpose of producing a corrosion-resisting metal, came about without references to theory, as an empirical matter, and even now, although copper-bearing iron has been on the market for many years, and the fact of its resistance to atmospheric corrosion has become well known, nevertheless, theory to account for its behavior has not kept pace with practice and remains incomplete.

[10] William D. Richardson, A Suggested Basis for an Index of Corrosion for Iron and Steel, Proc. Am. Inst. Chem. Eng., 1920 13, Part 1, 277.

The names and dates associated with the development of copper-bearing iron are as follows: F. H. Williams, 1900,[11] Stead & Wigham, 1901,[12] Breuil, 1907,[13] W. H. Walker, 1911,[14] D. M. Buck, 1913,[15] D. M. Buck and J. O. Handy, 1916,[16] E. A. and L. T. Richardson, 1916,[17] Kalmus and Blake, 1917,[18] O. W. Storey, 1917,[19] D. M. Buck, 1919,[20] S. M. Hoyt.[21]

As the result of many exposure experiments by different investigators, the conclusion seems warranted that any of the ordinary varieties of iron with the addition of from 0.10 to 0.50 percent copper are more resistant to atmospheric corrosion than without this addition. Fortunately the working properties of the metal are not greatly or at all affected by the presence of small amounts of copper.

It has been observed that the presence of arsenic, antimony or copper in sulphuric acid used for "pickling" causes retardation of the "pickling action.[22] It should be recalled in this connection that a few years ago "copper" nails and other builders' hardware were in favor on account of their alleged corrosion-resisting properties. A little light has perhaps been thrown on the influence of copper by experiments reported before this Society at the Cleveland meeting last year.[23] It was shown when copper is added to normal hydrochloric and sulphuric acids in the proportion of 10 grams metallic copper per 100 liters, that none of the ordinary varieties of rolled iron plates showed any appreciable change of solution rate from that in the normal acids without this addition. On the other hand, in nitric acid the rate of solution for the same metals was catalyzed negatively, so that in the presence of copper the rate was lowered to about two-thirds the

[11] Iron Age, November 29, 1900.
[12] Journal, Iron and Steel Inst. (1901), 2, 135.
[13] Journal, Iron and Steel Inst. (1907), 2, 41 and 60.
[14] Proc. Am. Soc. Test. Mat. (1911), 2.
[15] "Copper in Steel—The Influence on Corrosion," J. Ind. Eng. Chem., June, 1913.
[16] "Research on the Corrosion Resistance of Copper Steel." J. Ind. Eng. Chem., March, 1916.
[17] "Observations Upon the Atmospheric Corrosion of Commercial Sheet Iron." Trans. Am. Electrochem. Soc. (1916), 30, 379.
[18] "Corrosion of Ingot Iron Containing Cobalt, Nickel or Copper." Proc. Am. Inst. Chem. Eng. 1916, 9, 233.
[19] "The Corrosion of Fence Wire," Trans. Am. Electrochem. Soc. (1917), 32, 285.
[20] "The Influence of Very Low Percentages of Copper in Retarding the Corrosion of Steel." Am. Soc. for Test. Mat., June, 1919.
[21] "Exposure Tests of Sheeting Materials," Chem. and Met. Eng., August 1, 1919.
[22] Cushman, Discussion of D. M. Buck's paper, A Review of the Development of Copper Steel, Am. Iron and Steel Inst., 1920, 389.
[23] William D. Richardson, The Solution of Metals in Acids as Related to Corrosion, Trans. Am. Electrochem. Soc. (1920) 38, 245.

rate without copper. On the other hand, when cast-iron or semi-steel were subjected to the same treatment in nitric acid, the rate was catalyzed positively and on the average was approximately doubled. The negative catalytic effect of copper on the solution of the rolled metals in the oxidizing acid is of the greatest interest. The observation in connection with "pickling" noted above was not confirmed in the case of the non-oxidizing acids, hydrochloric and sulphuric. The fact that copper catalyzes the rolled metals negatively in the presence of an oxidizing acid may prove of special importance if this fact can be correlated with the observed behavior of copper-bearing iron under atmospheric corrosion. There is another factor, however, to be taken into consideration; namely, the relationship of the products of corrosion to the metal. All observers agree that the rust formed on copper-bearing iron adheres more closely under atmospheric corrosion than on other test plates free from copper. Little is known of the reasons for rust adherence or non-adherence to different kinds of iron and steel undergoing corrosion,[24] and, generally speaking, theory is all but wanting for the behavior of copper-bearing iron under atmospheric corrosion. As is the case with so many other examples, the basic properties of the metals concerned and their alloys in relation to hydrogen and oxygen under the conditions of corrosion have not been precisely determined.

SILICON-CONTAINING CAST IRON.

Just as the empirically-produced copper-bearing iron occupies a unique position among the rolled irons and mild-steels for its corrosion-resisting properties, so does silicon iron among the cast metals. Cast iron rich in silicon as a corrosion- and acid-resisting alloy was also produced empirically and without reference to theory. The names associated with this alloy are as follows:

1. Mallet, "British Association Reports" (1838), 277.
2. Turner, "Metallurgy of Iron," p. 421. Pub. by Chas. Griffin & Co., 1908.
3. Jouve, "J. Iron Steel Inst." (1908), III, 310.
4. Vigouroux, Bull. Soc. Chim. (1914), **15**, 268.
5. Charpy and Cornu, Bull. Soc. Chim. (1914), **15**, 497;

and a number of manufacturers of silicon-iron appearing under

[24] Experiments on the Corrosion of Iron and Steel, William D. Richardson, Proc. Am. Inst. Chem. Eng., 1920 **13**, Part 1, 169.

proprietary names "Tantiron," "Ironac," "Duriron," etc., during recent years.

The alloys at present on the market generally contain about 15 percent silicon, although maximum resistance to solution in acids is practically reached with a 20 percent alloy. Unfortunately, silicon in the considerable proportion necessary to produce an acid-resistant alloy, does seriously modify the working properties of the metal, and the resultant product is extremely hard and brittle. This alloy shows its greatest resistance to nitric acid, next to sulphuric, least to hydrochloric among the common acids and this fact would seem to indicate that the factor which I have termed the oxygen influence[25] is decisive in determining resistance to corrosion in this instance.

The following experiments with silicon-iron alloy afford additional evidence on this point.

BEHAVIOR OF DURIRON.

Duriron is commonly supposed to be an alloy of cast iron and silicon containing about 15 percent of the latter element. It is not subject to natural corrosion in water or salt solutions and is not readily attacked by the common acids, hydrochloric having more effect, however, than nitric or sulphuric. When coupled with pure open-hearth iron in a simple cell containing sodium chloride solution, it is at first strongly electro-positive to the pure iron. The difference in potential, however, soon diminishes to a more or less constant voltage. The high initial difference in potential is evidently due to an oxide film of some sort on the Duriron. After the voltage has once dropped it does not rise again after moderate exposure to the air.

In sodium sulphate solution the same general phenomena are observed.

In dilute sulphuric acid, however, the behavior of Duriron is different. At first strongly electro-positive to pure iron, the difference of potential drops rapidly to zero and thereafter the Duriron becomes increasingly negative to the pure metal. If both poles are simultaneously lifted into the air and re-immersed in the acid, a temporary increase in the difference of potential occurs, the pure iron being electro-positive.

[25] Solution of Metals in Acids as Related to Corrosion, William D. Richardson, Trans. Am. Electrochem. Soc. (1920) 38, 245.

Duriron is electro-negative to nickel, lead, copper and carbon, and electro-positive to zinc and aluminium. The behavior with aluminium, however, requires further comment. In neutral NaCl solution aluminium is electro-negative to Duriron. The same is true for dilute hydrochloric acid. In sulphuric acid this relationship holds temporarily, but the difference of potential gradually drops to zero and remains there. The same is true for nitric acid, but in nitric acid equilibrium is reached somewhat more quickly than in sulphuric. In neutral sodium sulphate the same behavior holds as for sulphuric and nitric acids. In acetic acid likewise no difference of potential is shown.

In dilute nitric acid wherein the "no potential" phenomenon is most marked, the observed phenomena are no less than astonishing. So far as the galvanometer needle indicates, one might be dealing with electrically inert substances—pieces of wood or glass. This appears to be passivity induced in dilute nitric acid. One is reminded of Faraday's words:[26] "The oxidized iron wire of Professor Schoenbein is, when in association with platina, exactly as another piece of platina would be. There is no chemical action or any electric current." It may be that the explanation of this curious behavior must be sought in the formation of an oxygen layer of some sort both on the aluminium pole and Duriron pole.

In a previous paper[27] attention was called to the unusual behavior of the aluminum-iron couple in nitric acid as compared to the same couple in hydrochloric acid. It was shown that in nitric acid aluminium was frequently electro-positive to iron but that this did not hold in hydrochloric acid since the halogens are always antagonistic to the oxygen effect. Thus, aluminium in the presence of an oxidizing acid behaves as a noble metal, only losing its "nobility" or passivity in the presence of halogens just as the noble metals themselves do.

NICKEL- AND NICKEL-CHROMIUM STEELS.

Nickel steel was manufactured and used in the beginning primarily for its physical properties unrelated to corrosion, but latterly nickel-steel alloys, especially those containing a considerable portion of nickel, have been used on account of their resistance

[26] Phil. Mag. (1836), 9, 53.

[27] Solution of Metals in Acids as Related to Corrosion, Trans. Am. Electrochem. Soc. (1920), 38, 245.

to corrosion. This resistance appears to increase with increasing proportion of nickel up to about 18 percent, which produces an alloy which may be regarded as practically non-corrodible under ordinary atmospheric conditions. "Invar," containing about 36 percent of nickel, 0.5 manganese and 0.5 carbon, has been highly recommended for the manufacture of precision and various physical instruments on account of its non-corrodibility as well as its very low coefficient of expansion. Ordinary nickel steel contains up to 3.5 percent of nickel and would be expensive to manufacture as a corrosion-resisting metal in competition with copper steel, unless from natural iron ores carrying a suitable percentage of nickel. While considerable data is at hand bearing on the corrodibility of this type of steel, much more information is necessary before final judgment can be passed on its resistance to corrosion. After corrosion has once started it appears to proceed at an increasing rate, so that long exposure tests have not borne out the promise of those of shorter duration.[28]

Chromium is often used with nickel, proportioned to about one-third of the latter. Such steels are said to resist corrosion in a manner similar to the nickel steels, but more exact data on this point are needed.

NICKEL-COPPER STEELS.

Copper has been used to replace a portion of the nickel in nickel steel without greatly affecting either physical or corrosion-resisting properties. Studies in this case also are incomplete or wanting. It might be expected that nickel-copper steel would resist atmospheric corrosion better than nickel steel.

CHROMIUM STEEL.

The resistance to corrosion conferred on iron by such metals as nickel, cobalt and chromium, which themselves have little tendency to corrode, appears to be an additive property. No new and unexpected or extreme and unusual corrosion resistance is given by small or large additions. In general, the corrodibility declines with increasing amounts of the alloying element until a minimum is reached. Chromium has been used in conjunction with iron in the corrosion-resisting field chiefly in the production of the type of steel known as "stainless," containing about 12

[28] Friend, Bently and West, Trans. Iron and Steel Inst., May, 1912, 85, 249; Proc. Inst. Metals, 1913 87, 388.

percent chromium. Complete data as well as theory are lacking for alloys of this type. However, they do not corrode readily under ordinary atmospheric conditions or when treated with dilute acids.[29]

NICKEL-COBALT-CHROMIUM ALLOYS.

The alloys produced from these three metals in various combinations are well known to have high corrosion-resisting properties as well as important physical and electrical properties. Theory in connection with their behavior is wanting, although in the main their corrosion resistance appears to be additive. Naturally the high cost of these alloys restricts their use to a few purposes. Perhaps the best known of the cobalt alloys is the Stellite developed by Mr. Haynes, of Kokomo, Indiana, and manufactured at Deloro, Ontario.[30]

CONCLUSION.

It would require a rash prophet to predict what future course the development of corrosion-resisting ferrous metals would take, but it may not be amiss to indicate the direction suggested by our present very incomplete co-ordination of theory and facts with respect to corrosion. Because oxygen is the dominating influence in ordinary corrosion it would seem necessary, in order to convert its malign effect into a benign one, either to employ it under controlled conditions as an anti-corrosion agent, or to offset its influence by modifying the composition of the metal or by preventing its access. These general methods are shown in tabular form below.

1. *Prevention of Corrosion by Utilization of the Oxygen Influence:*

(a) By maintaining a passive surface.

(b) By means of adherent rust or adherent magnetic oxide.

2. *Prevention of Corrosion by Avoiding the Oxygen Influence:*

(a) By changing the composition of the metal so that the oxygen influence is of no effect.

(b) By means of protective coatings, paint, varnish, lacquer, etc.

[29] Sir Robert Hadfield, Corrosion of Steel Alloys, Trans. Faraday Soc. (1916), **11**, 183.

[30] Trans. Am. Electrochemical Soc. (1920), **37**, 507.

The maintenance of a passive surface may be said to be difficult of accomplishment but not necessarily impossible. There is a considerable analogy between the passive surface of iron induced by strong oxidizing agents, such as nitric and chromium acids, and the ordinary surface of aluminium, chromium, nickel, cobalt and the noble metals.

The relationship between composition of metal and adherence of rust is unknown, but two examples offer a possible clue. First, copper-bearing steel appears to produce an adherent layer of rust, and second, cast iron does also. In the latter case the rust adhesion may be due to the presence of graphitic carbon.

Naturally any effect looking to the avoidance of corrosion necessarily depends upon suitably modifying the composition of the metal. It may be possible, however, to so modify the compositions specifically that the oxygen influence is avoided. It may be this result which is attained when iron is alloyed with nickel and cobalt, but we cannot be certain at present that this explanation is correct.

The protection against corrosion by the old and time-honored methods of protective coatings need not be discussed here.

DISCUSSION.

F. N. Speller[1]: It may seem that the electrolytic theory fails when we consider the fact, referred to by Mr. Richardson and proven by many years of experimenting, that composition has no relation to relative corrosion of iron or steel and that efforts to obtain a corrosion-resisting alloy of iron have failed, at least with respect to corrosion under water or in systems containing a limited amount of free oxygen. As to the first of these apparent inconsistencies it has been impressed on me for many years that the surface condition of iron has manifestly so much influence on the rate and character of corrosion as to overpower any variation in composition which is possible in commercial practice. Following this lead which is right in line with the electrolytic idea of corrosion we trace the cause of pitting in pipes in most cases to the heavy magnetic oxide of iron formed in the process of welding.

In 1918, Mr. J. O. Handy and the author made some tests on

[1] Metallurgical Engineer, National Tube Co., Pittsburgh, Pa.

hot water pipes from which a portion of the mill scale had been removed. The depth of corrosion as found by measuring the deepest pit in the scale-free area was only 20 percent of that in the other portions carrying scale. The British Navy require all boiler tubes to be pickled free from scale and washed in lime water before use.

Based on much experience of this kind, I was permitted to carry out some experiments on removing scale from pipe on a large scale. The pipe was made about 10 percent larger than standard, cooled to 900° C. and rolled down to size in a train of circular rolls, which reduced the diameter and elongated the pipe, by which the brittle scale was broken loose. This was first put into regular use in one of our Pittsburgh mills in 1913. During the past year equipment was completed for so treating all butt-weld pipe. This thin scale which forms below 850°-900° does not adhere closely and appears to have much less influence on pitting, and can be readily removed by a few minutes' pickling if desired.

If we have no encouragement from the electrolytic theory to look for a non-corrodible alloy, we must give this theory credit for guiding us to the control of corrosion in closed systems by removal of oxygen, which I have described in detail in another paper at this meeting. This remedy holds even though the surface of the metal carries mill scale or is in contact with copper or brass; so that it may be said that with most domestic waters corrosion may be practically eliminated by removal of the dissolved oxygen. It is very difficult to remove the last trace of oxygen, hence a slight corrosion of insignificant amount is still found. When a better explanation of the mechanism of corrosion is found we may bid an affectionate farewell to this theory, which has served us so well in many cases.

Mr. Richardson, although ten years late, has contributed a touching swan song to the life-long discussion on the relative corrosion of iron and steel. The conservative conclusion seems to be that in general there is no difference between corrosion of wrought iron or steel except that in the atmosphere the copper contents of each controls the balance. This is sufficient, and all that was contended for in the case for steel.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

ANOMALIES ENCOUNTERED IN A STUDY OF IMMERSION TESTS OF IRON AND STEEL.[1]

By Allerton S. Cushman[2] and George W. Coggeshall.[3]

Abstract.

A plea for considering all possible factors when comparing corrosion tests of iron and steel, on the ground that there are in reality so many and so obscure variables that it is very easy to draw wrong conclusions. Change of rate of corrosion is also frequently met with, so that extrapolations of short-time results are often in error. One anomaly is due to very local corrosion, where the loss in weight over a large surface may be quite small, and yet failure occurs due to highly localized pitting; on the other hand, weight loss may be higher and yet so uniformly distributed that it counts as relatively unimportant. Tests in aluminum sulphate solutions, giving curious colloidal gels, are described. The author denies the protective action of copper in steel.—[J. W. R.]

INTRODUCTION.

One of the writers has frequently given expression to his doubts as to the reliability of corrosion tests of metals in which the conditions of exposure do not, and cannot be expected to, simulate the conditions met with under the multiform and complex attacks made on metals in service. Every careful student of corrosion problems has called attention to the fact that the course of the electrochemical reactions under which corrosion proceeds leads to a delicate and complex equilibrium which is indeed the resultant of a number of contributory causes, some of which may be known, some obscure, and some quite unknown.

[1] Manuscript received March 16, 1921.

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All the results of corrosion tests, which fill a rapidly growing literature on the subject, seem to the writers to accentuate the importance of interpreting the data most conservatively as applying only to the special conditions under which any given set or group of tests are carried out.

Everybody who has studied this subject knows that the progress of corrosion under any given set of conditions is affected not alone by the chemical but also by the physical make-up of the test pieces. In other words, although we may concentrate our attention on the chemical constitution of a group of metals which we are studying, we must also take into consideration the surface condition as comprised in the terms "hardness" or "softness," "roughness" or "smoothness," "stress" and "strain" (anneal), "segregation of impurities," and, above all, "density and homogeneity" as represented by the quantity and condition of the ever present gas content which may be present as (*a*) combined (*b*) in solid solution, or (*c*) in openings such as blow-holes, pockets, seams, and pipes. Again, we have to consider the attacking media, whether air or water, or both in alternation or combination, whether the reaction is acid, alkaline, or neutral, whether the media contain natural or earthy salts, or the products of human or industrial activities, whether the attacking media contain certain types of organic matter in solution, and, above all, the activity of dissolved oxygen and the electrochemical conditions in general.

Certainly no one can deny that the progress of corrosion is primarily dependent on the solution tension of the contact surface of a given metal with the attacking medium, whether this be a damp atmosphere or some sort of liquid. The solution tension may or may not remain constant during any given period or change in conditions. The progress of corrosion may speed up or slow down as time passes and conditions change. Catalytic effects may be paramount, while again catalytic poisons in the system may dampen these effects. There are some conditions which tend to produce a passive condition on a metallic surface, which means that solution tension is impeded or perhaps entirely stopped. Above all, it must be remembered that the solution tension on a contact surface of corrosion is never the same at all

points, so that a corroding member is never in electrochemical equilibrium, solution taking place with attendant loss in substance more rapidly at electropositive nodal points, as is shown by the "ferroxyl indicator." Again, we have over-voltage phenomena to take into account; a given surface may be polarized or plated with ionic hydrogen, or, in other conditions, it may be passive and plated with ionic oxygen, or hydroxyl. It is a very complex subject, the governing conditions of which are not as yet explainable by science. In the writers' opinion, the progress and governing of corrosion is more than an electrochemical problem within the ordinary scope of electrochemistry, but must be considered largely from the standpoint of the higher physics, which attempts to apply all that is known of the activities of the electrons in chemical reactions. In other words, up to a certain point we were satisfied with applying what we knew of the theory of solutions and the behavior of ions to our problem. Now we must go a step further before we can hope to furnish a satisfactory scientific explanation of many practical results which we obtain in these tests. It is because of the many-faceted prospect of the corrosion problem, that so often interpretations of the results of tests remind one of the story of the two knights of olden time, who engaged in combat over an argument as to the blazonry on a shield which each observed from a different viewpoint. In the same manner, we might engage in combat because a certain type of metal which had given a good account of itself under test under one set of conditions fell down badly under another.

It is with no desire to enter the lists in any such combat that these notes on some observations made while conducting a great number of immersion tests, are offered at this time.

IMMERSION TESTS.

In conducting immersion tests, we may consider two separate types or conditions which we might define broadly as "busy" and "idle", although practically speaking these conditions often merge into each other. To illustrate our meaning, we might consider two metal tanks open at the top, in one of which a natural water was stored but rarely used, and the other in which a water supply was drawn from continuously and which was being constantly

filled with fresh water. No close student of corrosion problems would care to predict, if his reputation as an expert rested on the prophecy, which tank would fail first. A failure in a tank may be, and usually is, taken to be at the time when some little hole or number of holes let the water through, even though more than 99 percent of the metal structure has not suffered in the least. There are two opposing factors at work in such a system as we are imagining. The tank, which is continually receiving fresh water, is certainly also receiving fresh oxygen and probably, though not invariably, a fresh supply of hydrogen ions contributed by carbonic acid or other acid constituents. On the other hand, conditions in the other tank are quiescent so that electropositive points or nodes are apt to remain undisturbed and pit through to destruction more rapidly than in the moving system. The question is not how much rust is formed but how it forms, that will determine the life of the tank or any other immersion or semi-immersion system.

Now, the great question for discussion of recent years in regard to corrosion resistance, as far as the ferrous metals are concerned, is whether alloying copper with the metal up to about 0.15 to 0.25 percent is beneficial in conferring a certain degree of corrosion resistance.

From results of the Pittsburgh atmospheric tests of uncoated sheet metals, it may be inferred in a general way, in spite of some glaring exceptions, that the presence of a little copper as an alloying constituent lowers the solution pressure of the surface of the test piece, and thereby confers some measure of protection. The evidence on this point is confined, however, only to bare metal sheets exposed in an acid-bearing atmosphere, as is very carefully pointed out by Prof. O. Bauer of Berlin as the result of four-year exposure tests, under many different conditions of exposure in Germany.[4]

It is obvious to any unbiased mind that the conditions of an atmospheric test cover only a special set of conditions, which are not comparable to most of the conditions of service. Sheet metal is rarely if ever exposed to the weather in an uncoated condition. If the metal is not galvanized, it is at least painted, and

[4] Stahl und Eisen, Jan. 13, 1921, **41**, No. 2, 37-45; and Jan. 20, 1921, **41**, 76-83.

when a coating is applied, the solution pressure at all points on the surface is no longer a factor in corrosion resistance. Furthermore in other situations and conditions, the reactions of attack may change from acid to neutral or alkaline, or we may have to deal with partial or total immersion in the attacking medium. It is a fair question whether the alloying of small quantities of copper with steel under very many of these varying conditions is not actually deleterious and whether the conclusions that many people are drawing from the results of the American Society for Testing Materials, as well as other atmospheric tests, are not actually misleading. It is a fair question also, which has not yet been satisfactorily answered, as to just how copper as a constituent of iron or steel holds back the solution pressure of iron under exposure to an acid-bearing atmosphere. If the copper goes into solution proportionately as the iron ions pass in, and then tends to plate back again, it might under the circumstances retard or slow down the attack.

The more slowly a rust-coating forms over the surface of a steel exposed to the atmosphere the more fine-grained, dark-colored, and tightly-adherent it appears, and undoubtedly under the conditions of such a test this is beneficial. If, however, copper passes into solution and then tends to plate back, it certainly would in part find itself able to do so if the liquid phase which is an essential part of any corrosion system was sufficiently abundant and not too strongly acid, which it may not be in a bare weather test, where at no time is there present more than a very thin film of moisture. If in some other system copper does plate out, it should from the electrochemical viewpoint be very deleterious to the surface under attack.

The only way of gaining information in regard to such a moot point as this is to put the question to the test of experiment, which is much more satisfactory than merely theorizing about the subject. It is well-known that mercury will not amalgamate on a surface of iron or steel, but will readily do so on copper. It occurred to us, therefore, that if surfaces of copper-bearing and essentially copper-free iron and steel were separately immersed in dilute solutions of mercuric chloride, some information in regard to this question might be gained. This point will be taken

up in a later paragraph after a description of the test pieces used has been given.

DESCRIPTION OF SAMPLES AND TEST PIECES.

We have available a number of commercial sheets of about 26-gauge (0.47 mm. thick), from which to cut test pieces for a number of experiments which will be described. These available sheets are in part blue annealed and in part galvanized. It was found that large pressed-glass tumblers of about 350 cc. capacity could be purchased by the gross at a reasonable price, and it was determined to use these. These containers permitted cutting the test pieces to a size 2 x 3 inches (5 x 7.5 cm.), giving 12 square inches (75 sq. cm.) of contact surface, ignoring the cut edges. Such test pieces will weigh from 12 to 16 grams each, as the gauge, even in a single commercial sheet, is never quite constant at all points. In making the tests, the clean, weighed test pieces were placed in the tumblers in a slanting position and immersed in 300 cc. of the attacking solutions. A cover glass prevented undue evaporation, but did not prevent free access of air to the system. The metals used were characteristic of the three types generally known as copper-bearing steel (*Kb*), copper bearing iron (*Cb*), and commercial pure iron (*Ab*). The analyses of these metals, with their significations, are given below. The arsenic content is also given, in view of the fact that a disproportionate arsenic content might produce some anti-catalytic effect during the progress of corrosive reactions.[5]

	C	Mn	S	P	Cu	As
Kb	0.04	0.29	0.038	0.077	0.20	0.015
Cb	0.011	0.032	0.039	0.055	0.251	0.102
Ab	0.011	0.015	0.038	0.006	0.038	0.012

The question of the reactive surfaces of our test pieces was considered an important point, and one to which we gave much thought. Commercial sheets vary greatly in surface condition,

[5] As a matter of fact, the growing scarcity of the very highest grades of iron ore indicates that the arsenic content of steels should not continue to be ignored by metallurgists and metallurgical chemists.

and if blue annealed test pieces are pickled in acid in the laboratory, one set may be much more etched before the scale is all removed than another. Moreover, in a plan that contemplated, as ours did, engaging in hundreds, perhaps thousands, of separate experiments, the labor involved in pickling black sheet test pieces is almost prohibitive. We found that by selecting galvanized sheets of the different types, of as nearly as possible the same gauge and weight of coating, and then pickling all samples in concentrated hydrochloric acid until the zinc was all removed, we could get bright bare test pieces with little or no etching of the surface. In all our tests this method of preparing samples was followed.

TESTS WITH SOLUTIONS OF MERCURIC CHLORIDE.

With this brief description of the test pieces used, and the method of immersion, we may pass to the description of the critical immersion tests with solutions of mercuric chloride. Series were set out with two concentrations, one of *N/10* strength (about 1.36 percent), and the other 5 percent strength. The immersions were allowed to remain undisturbed for thirty days. In all cases some flocculent reddish yellow iron hydroxide was seen to form on the upper surface of the test pieces. At the end of the 30-day period all test pieces were removed for cleaning and inspection. They were washed in running tap water and scrubbed with a stiff tooth brush. The significant fact came out that in the cases of the *N/10* solution both the copper-bearing samples (*Kb* and *Cb*) were heavily amalgamated with bright mercury mirrors, while the substantially copper free (*Ab*) retained its characteristic gray iron surface. It was obvious that the corrosion weight losses could not be determined on account of the mercury mirrors on *Kb* and *Cb*. The corrosion weight losses in this 30-day test were of the same order of magnitudes and are not regarded by us as particularly significant, being very small in each case, although slightly larger for the copper-bearing steel. The significant point is that immersion in dilute mercuric chloride solutions shows that copper first passes into solution with the iron ions and then plates back and forms a mirror surface with the reduced mercury. Further comments on this result will be re-

served for discussion later on. In the case of the 5 percent solution, the corrosion was proportionately greater in each case. Reduction to metallic mercury occurred in every test, but the corrosion reactions were sufficiently severe so that the mercury mirrors were eaten into or etched off. *Kb* and *Cb* were badly pitted and eaten into, but only partially amalgamated. *Ab* was neither amalgamated nor pitted. Efforts were made to bake off the mercury from the amalgamated pieces, but as this superimposes oxidation and blueing of the surface, the weight loss relations were not considered by us as of any value on which to base conclusions. As might have been expected, however, the most deeply pitted and etched specimens indicated the highest weight losses. These tests are all being repeated and duplicated many times over and by several experimenters. The presentation must await the lapse of sufficient time to report them in detail.

If it is true that under conditions of immersion or partial immersion, as for instance in any case in which the attacking watery medium is in excess, copper passes into solution and plates out again, the presence of copper as an alloying constituent in iron or steel could not be considered beneficial from the electrochemical point of view. The iron-copper couple immersed in any electrolyte, whether a natural water or a chemical solution, must suffer damage by reason of electrolysis.

EXPERIMENTS WITH SOLUTIONS OF BICHROMATE.

In 1906[6] one of us had shown that the passivity produced on the surface of iron and steel by immersion in solutions of an alkali bichromate could be partially or wholly overcome by the addition of gradually increasing increments of a solution of a copper salt. It seemed to follow from this that if copper passed into solution from copper-bearing iron and steel it would require a more concentrated solution of bichromate to maintain passivity and non-corrosion in the cases of samples of copper-bearing metals *Kb* and *Cb* than it would in the case of low copper *Ab*. In order to put this question to test, solutions of potassium bichromate were made up beginning with *N/100* strength based on the oxidizing power of the salt as a maximum and passing on down by

[6] See "The Corrosion and Preservation of Iron and Steel." Cushman and Gardner. (McGraw-Hill Book Co.). Pp. 113-114.

successive steps in concentration, so that we had *N/1,000, N/2,000, N/6,000, N/8,000,* and *N/10,000.* By immersions of the three samples in these solutions it was found that in *N/100* strength all samples remained bright and uncorroded. In *N/1,000, Kb* failed to the rusting stage in a few days in one set of tests, but withstood attack in another. In *N/2,000, Ab* remained bright for the 30-day period, *Kb* and *Cb* showing much rust. It was not until the concentration of *N/6,000* was reached that *Ab* showed visible corrosion. *Kb* and *Cb* formed coatings of red rust in *N/2,000* solution, but were as a rule protected in *N/1,000* solution. Calculation based on a number of tests shows that 4 to 6 times more CrO_3 per unit volume is required to hold back the solution pressure and consequent corrosion in an immersion system of copper-bearing iron or steel, than is needed to protect iron essentially free from copper.

EXPERIMENTS WITH SOLUTIONS CONTAINING FERRI-CYANIDE.

Since all corrosion of iron and steel must be preceded by the entrance into solution of ferrous ions, it would appear that if ferri-cyanide ions were introduced into the reacting system the time factor and degree of blueing due to formation of Turnbull's blue would be an indicator of the solution pressure of different types of metal under test. Such an indicator would, however, be limited to systems in which ferri-cyanide ions did not react with other ions present. Copper-bearing iron and steel appear to produce blueness in *N/10* solution of potassium ferri-cyanide when low copper iron does not. This subject is being investigated more fully but is not yet ready for detailed report.

EXPERIMENTS WITH SOLUTIONS OF ALUMINUM SALTS.

Some time ago a correspondent asked for information in regard to the best type of metal of which to construct tanks for the storage of concentrated solutions of aluminum sulphate. Since there were no available data on the subject, a series of tests was projected. It was presumable that if a copper content tended to increase electrolytic corrosion under immersion conditions, it would be an undesirable constituent in a metal intended to withstand such an attack. A number of samples, including black,

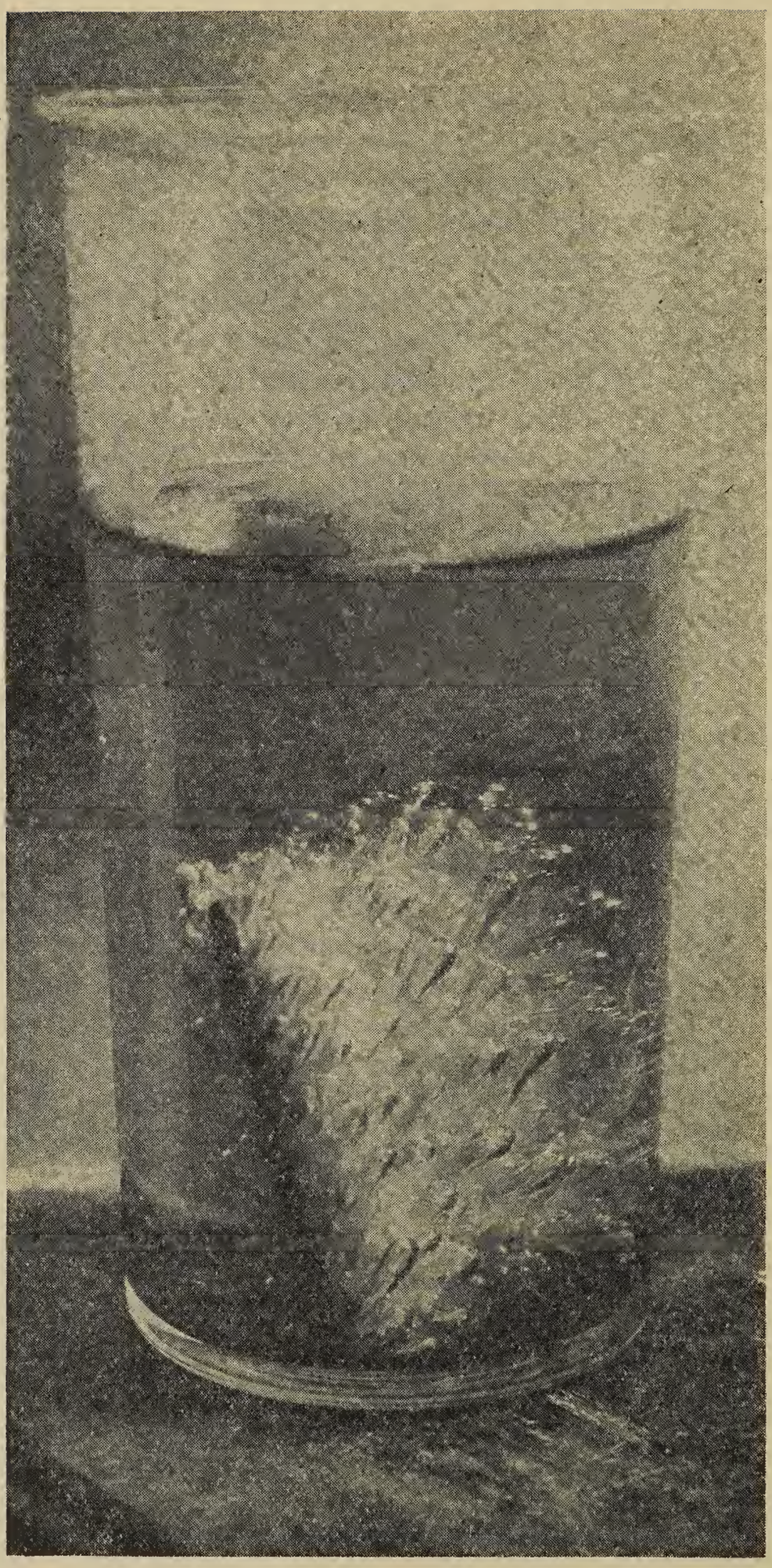


Fig. 1. A 2 x 2 inch (5 x 5 cm.) specimen of galvanized copper-bearing steel immersed in 20 percent aluminum sulphate solution. Showing the peculiar nature of the colloid gel formed as corrosion proceeds.

pickled and galvanized sheet, were prepared and immersed in 20 and 10 percent solutions of aluminum sulphate.[7] The preliminary tests were made by immersing black, ungalvanized test pieces in the solutions. Rather unexpected and somewhat extraordinary results were encountered, which are here announced for the first time.

After the lapse of from two to three weeks the liquids in the case of the copper-bearing steel tests suddenly solidified into a gel of aluminum hydroxide. Aluminum sulphate in solution hydrolyzes to an acid reaction. If unpickled samples of iron and steel are immersed in such a system, iron ions will pass into solution and further hydrolysis will take place, until under the influence of solution tension the iron ions gain on the free acid ions; the basicity will then reach a point where solution of aluminum and ferrous sulphates can no longer be maintained and the system suddenly turns to a hydroxide gel.[8]

After the gel is formed in a test of this kind, the metal plates can be removed for cleaning and weighing. In some cases the metal plates are found to be pitted through in segregated pin-holes or even reduced to a curious lace-like consistency. When the test was repeated with carefully pickled and cleaned test pieces, little or nothing happened in most cases, even over a thirty-day immersion period. It appears the corrosion reactions require some catalytic starter, possibly mill scale in this case, and that once started they proceed steadily to the gel point in the more concentrated 20 percent solutions. In the cases of the more dilute 10 percent concentrations gels do not as a rule form. Whether the reactions will proceed to the total destruction of the test piece is a function of time and equilibrium between the surface area of the test piece and the quantity of the solution or liquid phase present.

It is, however, when we immerse galvanized samples of the various types of iron and steel in 10 and 20 percent solutions of aluminum sulphate that the most unexpected results are obtained. The corrosion reactions start off apace in both concentrations, hydrogen is disengaged, and if gels finally form they take on a

[7] In all cases either Baker's or Baker & Adamson's c. p. chemicals were used, and the concentrations refer to actual quantities of $Al_2(SO_4)_3$ without reference to the water of crystallization.

[8] Similar results can be obtained much more quickly when metal turnings rather than metal plates are used, but in this case the effects produced have no comparative value on account of the unknown surface areas of the samples exposed.

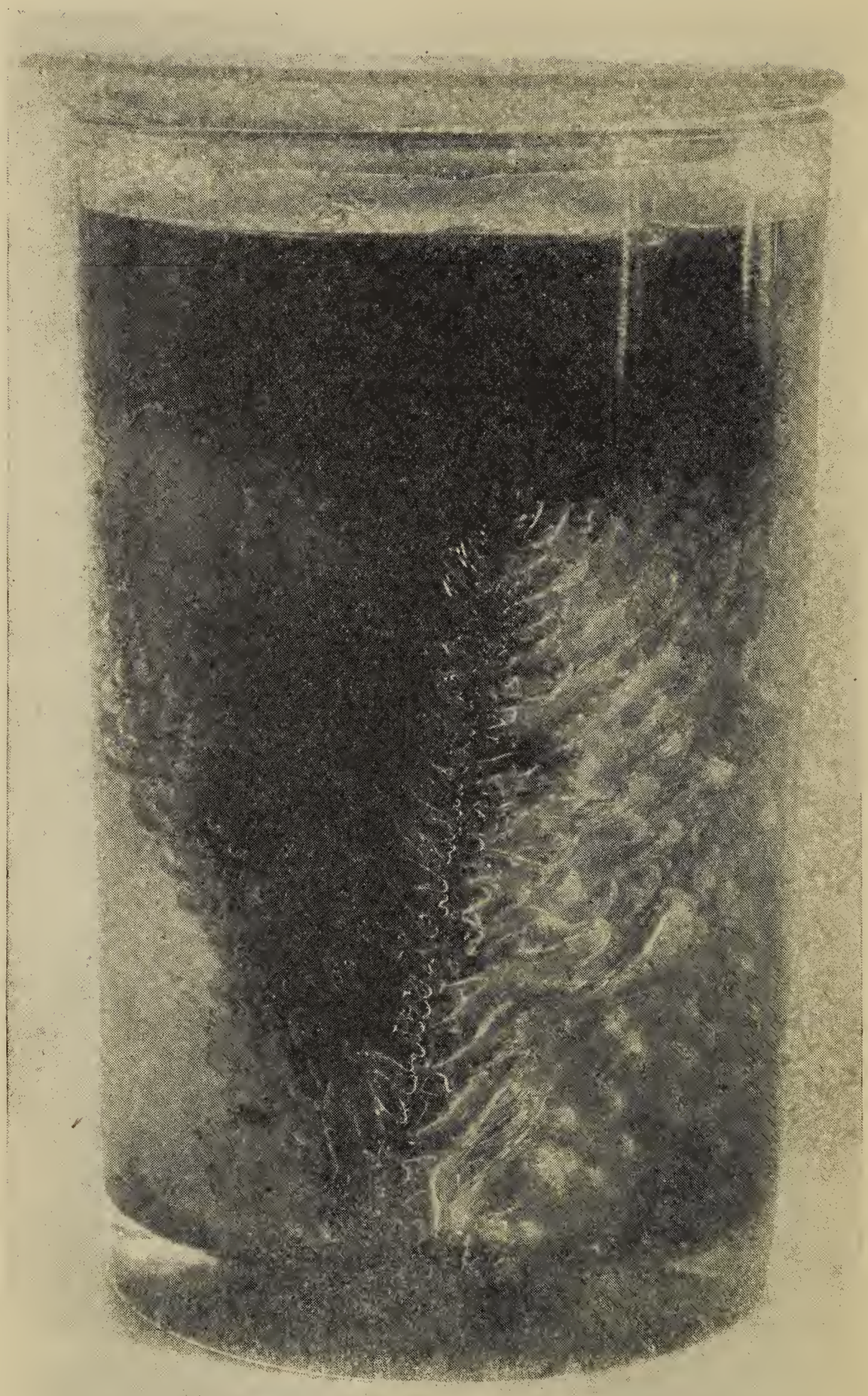


FIG. 2. Two test pieces of galvanized copper-bearing steel *Kg* after two to three weeks' immersion in 20 percent aluminum sulphate solution. Showing the curious gel formed as corrosion proceeds.

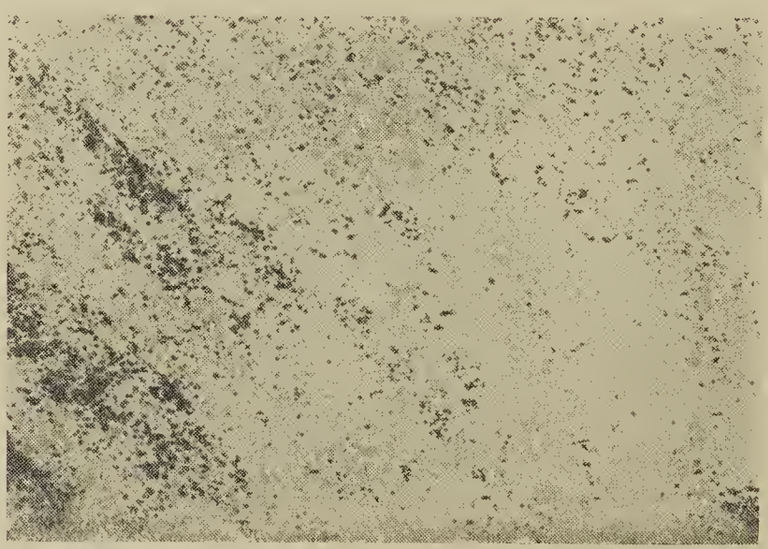
most extraordinary appearance. The colloid gel forms in a cluster of bulbous, tubular processes much like an organic fungoid growth (Figs. 1 and 2). In other cases under observation, in 10 percent concentrations, the reaction slows down as soon as the zinc coating has been stripped from the "pure iron" samples, but in the cases of the copper-bearing samples the reaction continues until not only the zinc coating but the ferrous base metal itself has been entirely dissolved. In some cases the result has been obtained in from two to three weeks, on 26-gauge (0.47 mm. thick) test pieces.

These results were so surprising that the authors would have hesitated to publish them if it were not for the fact that they have been repeated a sufficient number of times to insure their accuracy. It is very strongly indicated that the copper-steel samples, whether black or galvanized, corrode more easily and much faster in immersion tests of this character than does low-copper iron. The authors were puzzled by the very unexpected fact that galvanized metal under the conditions of this test suffered far more than black samples, while pickled and cleaned samples suffered little or no damage even after the lapse of 60 days. Every possible explanation was canvassed. After discussion, it seemed a possible explanation to assume that since the zinc coatings passed readily into solution, forming zinc sulphate, the presence of copper was able to catalyze the formation of double sulphates of zinc and iron, thereby leading on to destruction of test pieces which contained copper. In the cases of the black samples in which no zinc sulphate was formed, the reaction proceeded along quite other lines. Obviously the best way to test this assumption was to start with pickled test pieces and add to the 20 percent solution of aluminum sulphate a quantity of zinc sulphate equivalent to the amount of zinc sulphate which would be formed from the known weight of zinc on the galvanized samples. This was done, with the result that in 21 days samples cut from low copper, *Ab,* were still clean and unetched, having suffered an average loss of 0.06 oz. per sq. ft. (18.3 g. per sq. m.) of surface. Samples cut from copper-bearing *Kb* had lost 3.20 oz. per sq. ft. (976 g. per sq. m.) or about 20 to 26 percent of their original weight, and were full of holes, similar to *Kb* test piece shown in Fig. 3. It seemed from

the result obtained that our assumption as to the effect of copper on the progress of the reaction was correct.

Ab
Pure Iron Substantially Copper-free.

Cb
Copper-bearing Pure Iron.



Kb
Copper-bearing Steel.

FIG. 3.

In the course of these investigations the authors had noticed that if the temperature of a 20 percent aluminum sulphate solution was raised to about 70° C., gas appeared to be vigorously dis-

engaged from the surfaces of pickled test pieces, which showed little or no action under immersion at laboratory air temperatures. This observation led to a series of boiling tests in 10 and 20 percent solutions of aluminum sulphate which checked up in a general way with the results obtained in cold tests. Tests were made on 26-gauge (0.47 mm.) pickled test pieces boiled in open beakers for periods varying from 14 to 30 hours, loss by evaporation being made up with distilled water. The results of one 14 hours' boiling test in 20 percent solution are shown in Fig. 3. The copper-bearing steel was reduced in a 30-hour test in 10 percent solution to an extraordinary lace-like condition after having lost about 5 oz. per sq. ft. (1,525 g. per sq. m.) of surface, or something over 85 percent of its original weight. In the same time the *Ab* sample lost about 2.5 oz. (763 g. per sq. m.) or about 44 percent of its original weight, while only a few fine pin-holes were developed.

It suggested itself to us after watching the progress of these interesting reactions that by boiling samples of copper-bearing steel of known copper content in 20 percent solutions of aluminum sulphate for a certain length of time and then re-analyzing the remaining metal, it would be possible to tell to what extent the copper passed into solution with the iron and to what extent it tended to plate out or be held back by the electrochemical effects. The original sample of 26-gauge *Kb* carried 0.20 percent copper and was used for experiment. After boiling 18 hours, the sample was removed, washed thoroughly, dried, and re-analyzed. It was found now to contain 0.35 percent copper. There are only two possible explanations of such a result that occur to us. Either the iron was selectively dissolved concentrating the copper content, or else both metals passed into solution in their quantitative rates, whereupon 20.5 percent of the copper in solution plated back. In any case we have another indication of the selective or segregated action of copper in copper-bearing steel under immersion conditions.

Aluminum chloride also hydrolyzes in solution to an acid reaction, but it is noteworthy that its action on the various types of metal is by no means as vigorous as aluminum sulphate solutions of equivalent strength, either hot or cold. The full results of tests must be reserved for report in a later paper. In general it

may be stated, however, that, as in the tests with aluminum sulphate, the ratio of attack in aluminum chloride solution is from two to three times greater on the copper-bearing metals than on the pure iron.

ACID TESTS.

It has been generally believed for some time past that a copper-bearing metal would stand a dilute sulphuric acid test better than a low-copper steel or iron. We therefore made an investigation of the effects of the three mineral acids in varying strengths upon the samples of the three types of metal in hand. The tabulated results would fill up several pages of print, and are only offered in summary at this time. On our samples, arsenic-free sulphuric acid in from 1-3 to 1-5 dilutions by volume on the c. p. concentrated acids acted slightly more vigorously on low-copper *Ab* than on copper-bearing *Kb* and *Cb* samples, although this was not always shown in long-time tests, even when the supply of acid was renewed from time to time. In more concentrated as well as in more dilute solutions the action was slight and there was little difference in resistance of the different types. In concentrated sulphuric acid, as would be expected on theoretical grounds, almost no attack was made on any of the test pieces. In pure concentrated hydrochloric acid the results are quite different. *Ab* is attacked very little in the cold, while *Kb* is vigorously acted on. In a 24-hour test, *Ab* lost 0.28 gram while *Kb* lost 2.27 grams, or about ten times as much. In 13 days, or 312 hours, *Ab* lost as much weight as *Kb* lost in 24 hours, while *Kb* lost about 50 percent in weight and was reduced to a skeleton lace-like appearance.

It was thought that slight differences in the surface smoothness of the two samples might account for this difference in reactions, since a rougher surface might furnish more points from which hydrogen could depolarize and thus the solution pressure would be speeded up, quite irrespective of the chemical constitution of the respective samples. In order to test this point, the surfaces of samples were deeply scratched and scored with a new file. Tests repeated with these samples, however, showed the same ratio of resistance to attack as in the preceding series. In dilute hydrochloric acid (1-2 by volume) the action is slower in the cold but

the ratio between low-copper *Ab* and copper-bearing *Kb* is maintained. In more dilute HCl (*N/100* and less) the attack was very slight on any of the samples. In concentrated nitric acid we face a condition of electrochemical passivity. Nevertheless, in the course of time, up to 30 days or more, it is possible to detect a very slight loss of weight in the immersed samples after removal followed by rapid but thorough washing in tap-water and drying. In this case, after 38 days *Kb* was the more resistant, as it lost 0.12 oz. per sq. ft. (36.6 g. per sq. m.), while *Ab* lost 0.90 oz. per sq. ft. (274.5 g. per sq. m.) of surface. In dilute HNO_3 (1-5 by volume) the resistance was reversed, for after 24 hours *Ab* lost 0.04 oz. (12.2 g. per sq. m.), while *Kb* lost 0.66 oz. per sq. ft. (201.3 g. per sq. m.) of surface. At the end of 120 hours both *Ab* and *Kb* had entirely disappeared.

Acid tests are very sensitive to a great number of electrochemical variables, and it is doubtful if any very definite conclusions based upon them will ever be justified. Our tests were made in good faith, and in order to gain such information as it was possible to obtain under the simple conditions of quiescent immersion of our samples. Our results do not agree with those published by W. D. Richardson[9] and are quite in contradiction to the results published recently by Bell and Patrick[10] and which were based on a most elaborate and careful scientific laboratory research. But these very discrepancies are a matter of great scientific interest in showing the sensitiveness of equilibrium of these electrochemical reactions.

Bell and Patrick worked on artificial alloys melted down in an Arsem vacuum electric furnace, and their iron base was as nearly as possible freed from all the ordinary impurities, both solid and gaseous, found in commercial metals. On the other hand, our tests were made on the very metals sold to consumers for construction purposes. Bell and Patrick found that copper alloyed with pure iron had a restraining influence on the solvent action of fairly strong hydrochloric acid in proportion to the amount of copper present, but were much surprised to find that the results in sulphuric acid refused to fall in line with any theory built up

[9] Rates of Solution of Iron and Steel in Non-oxidizing and Oxidizing Acids. W. D. Richardson, Amer. Inst. Chem. Eng., June, 1920.

[10] The Influence of Copper on the Rate of Solution of Iron in Acids. F. K. Bell and W. A. Patrick. Jour. Am. Chem. Soc., March, 1921.

on the hydrochloric acid action. We, for our part, found that independently of the question of whether the surfaces of the samples were rough or smooth, our copper-bearing steel was very visibly more corroded than our copper-free iron in any unit time. This can easily be seen by the way hydrogen sweeps off from the competing specimens, without waiting to determine weight losses.

MISCELLANEOUS TESTS.

In addition to the tests on which our preliminary notes have been given in the previous paragraphs, we have over eight hundred quiescent immersion tests under continuous observation. These tests comprise immersion in all conceivable solutions of varying concentrations that at one time or another might or have come into practical or service contact with iron and steel. All the results will be later tabulated and discussed in a paper which will from its very nature be so detailed and extensive that it will take much time and labor to prepare.

So far, from all the observations and recorded data obtained to date on immersion tests, we are obliged to conclude that wherever and whenever copper as an alloying constituent in steel does not show itself to be inert, it shows itself to be deleterious and in some cases dangerously so. We frankly admit that our results apply only to quiescent or what we have denominated in the introduction as "idle" immersion tests. Nevertheless we believe that they constitute a very real contribution to the general study of an interesting and important problem. Many engineers have jumped to the conclusion, since bare sheet metal weather exposure tests in Pittsburgh indicated that copper has a restraining action under such conditions, that copper should be a universally specified constituent of steel intended for all structural purposes. Prof. W. H. Walker has plainly so stated in his discussion of Mr. D. M. Buck's paper before a recent convention of the American Iron and Steel Institute. We do not hesitate to state that we believe that such conclusions are unconservative and that the results of investigations now being carried on in Germany, England, the Philippines and Australia, to mention only those that are known about, should be awaited and collated before general specifications are tampered with.

Quite aside from the scientific questions involved in these dis-

cussions, and differences of interpretation and opinion, there is involved a certain responsibility to the general metallurgy of the future. Our present, and in all probability to an increasing degree our future, steel-making processes must be in line with conservation of our national resources. In other words, our furnaces must use scrap as well as pig iron and ore. Copper is not eliminatable in iron and steel smelting, so that if copper-bearing specifications are to become general, there will be an inevitable tendency, with shrinking ore supplies, toward unavoidable high copper content in all commercial ferrous metals. If in the long run copper is proved to be deleterious for any considerable number of uses of iron and steel, our metallurgical descendants may well have reason to curse the era when fads were made a substitute for facts.

In concluding these preliminary notes on what is intended to be finally an exhaustive research, we have referred to the results we have obtained up to date, and we will be glad to assist in any possible way any investigator who desires to repeat or check up our results. In our opinion, when investigators disagree as to results, they should exchange their samples with one another. No investigator can speak with authority except with regard to his own available samples, and, as has been stated, so many variables affect the progress of corrosion reactions that absolute checking between the several workers in this field is almost impossible.

Washington, D. C.
March, 1921.

DISCUSSION.

A. S. Cushman: As the title of this paper indicates, I have not attempted to present to this Society the finished results of a long and tedious research, in the course of which some thousand tests have been kept under observation. I only here call attention to some results, which seem to be new. At least, as far as we are able to determine no such results have been reported by previous experimenters. It is perhaps well known that I am an opponent of the copper steel theory, as it applies to corrosion resistance in a general way.

The Pittsburgh test sheet showed crystals of ferrous sulphate accumulated on the underneath side, showing that sulphuric acid

had been a very decided factor in the corrosion and it always must be in bare sheet metal tests in such a smoky atmosphere as Pittsburgh, or in other places where there is smoke in the atmosphere. It would seem that there is a reason, perhaps not yet fully understood, why on an acid concentrating sheet (which is really a sheet exposed to the weather) copper content may be beneficial and still be harmful under other conditions. The rain and fog bring down little increments of sulphuric acid from the air, then the winds and sun evaporate the water—but we all know that sulphuric acid is not evaporable. Therefore, it must be con-

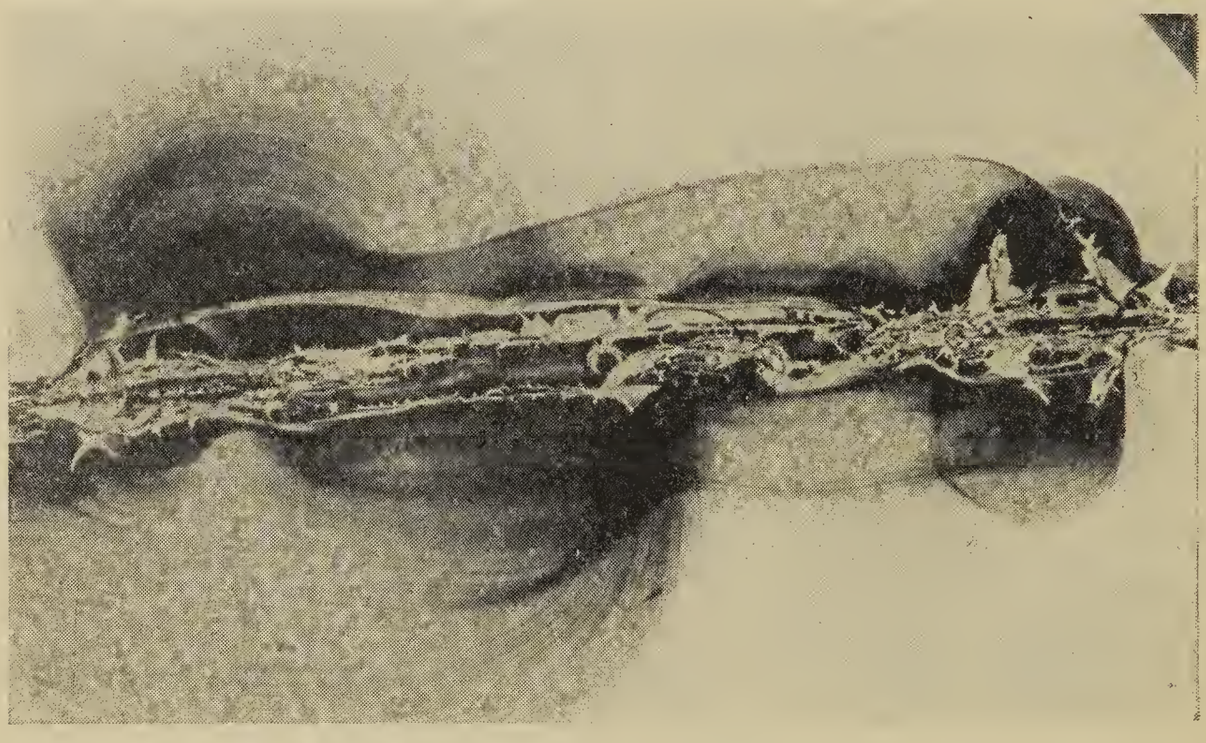


Fig. 4. Ferroxyl Test.

centrated on the surface up to a certain point, and that is the point where it begins most readily to neutralize itself at the expense of the underlying iron or steel.

Now, Mr. Buck has properly said that there is no commonly accepted explanation of why it is that copper as a constituent alloy, under such a test, seems to have a restraining influence on the rate of corrosion. When you immerse the same metals in acid solutions corrosion proceeds differently.

Wm. C. Moore[1]: This slide (Fig. 4) of Dr. Cushman's, showing lines of force, recalls to my mind the so-called Leisegang

[1] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.

phenomenon, which is frequently met with in colloid systems. Probably some of you have heard some of the talks by Dr. H. N. Holmes, of Oberlin University, on this subject, where he shows a number of tubes in which he has rings and bands of silver chromate, which were formed by the diffusion of a silver salt into agar-agar containing potassium chromate in solution. Possibly these lines of force are special cases of that same phenomenon.

COLIN G. FINK[2]: How do you explain it, Dr. Moore?

WM. C. MOORE: Diffusion through the precipitated colloid, I think, is the commonly accepted explanation of this occurrence of bands, but I have not followed the matter enough in detail to offer the most advanced explanation. The similarity of the striae mentioned, and the "lines of force" shown by Dr. Cushman, occurred to me at once, and I believe that it is not something peculiar to corrosion, but simply a colloid phenomenon.

COLIN G. FINK: Diffusion alone would not account for that because diffusion would be in a straight line. There must be another force in order to get the curvature.

J. W. RICHARDS[3]: That slide (Fig. 4) suggests to me that here is a visualization of the local currents, which we have all been talking about and believed to exist, but that they had actually been here photographed. I understand that the specimen had dried out, and that, therefore, the path of the currents from points of positive to negative potential had been petrified, as it were, showing visually the path of the electric current from positive to negative spots. The reason that those particles migrate is evidently that they are formed at one pole, and then they have been carried along by the currents along their path, and then having dried up the slide has visualized these local circuits which we talk about so frequently, but which I never saw before so plainly.

W. D. RICHARDSON[4]: While I was looking at Dr. Cushman's slides I was impressed by the same points which were brought out by Dr. Moore. I have seen this banding effect in ferroxyl experiments which I have made myself, but I noticed it mostly after the jelly had dried, and not while it was in a moist condition. I don't

[2] Consulting Electrometallurgist, So. Yonkers, N. Y.
[3] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.
[4] Chief Chemist, Swift & Co., Chicago, Ill.

want to say that the bands don't form while the gel is moist, but I noticed most frequently that after the drying they seemed to be more common. Those I have observed do not follow a direction from positive nodes to negative nodes, but rather form semicircles around the positive nodes, contrary to the assumption that Dr. Richards made, and I have been inclined to think, and do think now, that they are part of the banding phenomena which occur in jellies, such as agar and gelatine and glue, and are not essentially connected with electrolytic phenomena of corrosion.

A. S. CUSHMAN: I am not at all in opposition to the explanation that the effects shown are due to what has been called colloidal "rhythmic banding." But we do not yet know what this colloid banding is due to, and it may in itself be an electrolytic or even possibly an electronic phenomenon.

J. A. AUPPERLE[5]: The anomalies encountered in the study of immersion tests of iron and steel have been shown so well by the authors that what I have to add is a confirmation of the tests mentioned, and as some of my data were obtained by changing some of the details of the test, it may be of interest to refer to the results I have obtained.

Mercuric Chloride.

We used 16-gauge samples prepared by stripping black samples with the use of hydrochloric acid, and have obtained mirrors on copper bearing steel and not on the pure iron when these samples were immersed in the *N/10* mercuric chloride for 30 days.

We placed samples in separate tumblers in a 5 percent mercuric chloride solution at room temperature, using 200 cc. for each test. The test-pieces were removed every half hour, and the adhering mercury was dissolved by momentary immersion in concentrated nitric acid. The nitric acid dissolved the mercury very rapidly without attack on the iron or steel. After cleaning the samples in this manner they were again immersed in a fresh 5 percent solution of mercuric chloride, same being repeated twenty times, and at the end of the twentieth half hour immersion period we found, by weighing the samples, that the copper-bearing steel had lost approximately 20 percent more than pure iron.

[5] Chief Chemist, The American Rolling Mill Co., Middletown, O.

Aluminum Sulphate.

We have conducted many tests with the use of aluminum sulphate, using 20 percent of the anhydrous salt. Out tests invariably showed the copper-bearing steel to jelly in about one-fifth the time required for the formation of aluminum hydroxide jelly in the pure iron test.

Hydrochloric Acid.

We have conducted tests on 16-gauge samples which were immersed at room temperature in hydrochloric acid solutions of the following strengths: 0.1, 1, 3, 10, 20, and 38 percent.

In every instance we have confirmed the results obtained by Messrs. Cushman and Coggeshall, and have found the copper-bearing steel to be attacked to a greater extent than commercially pure iron. Copper steel lost approximately ten times as much weight as pure iron in the 38 percent solution of hydrochloric acid. These results are contrary to the results obtained by Bell and Patrick[6] who experimented with cast metals made from iron and iron-copper alloys. As Bell and Patrick did not give any analysis of the alloys, other than the copper content, it is very likely that the alloys contained appreciable quantities of carbon, as Kalmus and Blake[7], who made alloys along the same lines, obtained as much as 0.64 percent carbon in their iron alloys, which was likewise ignored by them in summing up their results.

A knowledge of chemistry is not necessary in order to show the increased rate of corrosion of the copper-bearing steel as compared with commercially pure iron when these metals are placed in separate vessels containing concentrated hydrochloric acid. Since the evolution of hydrogen gas is ten times more on the copper-bearing steel than on the commercially pure iron, the greater solubility of the copper-bearing steel is very apparent.

D. M. Buck[8]: So far as the controversy between pure iron and copper steel is concerned, I am perfectly willing to rest the case for copper on the observed facts as they are at present. I wish, however, to make brief reference to the test of Professor Bauer, as

[6] The Influence of Copper on the Rate of Solution of Iron in Acids. Frederick K. Bell and Walter A. Patrick. The Journal of the American Chem. Soc., March, 1921.

[7] Corrosion of Ingot Iron Containing Cobalt, Nickel or Copper. Herbert T. Kalmus and K. B. Blake. Am. Inst. of Chem. Engrs., New York City, January 10-13, 1917.

[8] Metallurgical Engineer, American Sheet & Tin Plate Co., Pittsburgh, Pa.

reported in the January 13th and 20th numbers of Stahl und Eisen, which tests have been quoted in Dr. Cushman's paper. It was found in those tests that in industrial air, copper steel showed somewhat less corrosion than what Professor Bauer terms non-copper steels, but in other conditions he did not find this difference. I have read Professor Bauer's paper and studied his tables very carefully. The fact that his tests did not show the same relative differences between copper steels and non-copper steels, as has been obtained by nearly all other investigators, is readily explained when we note that the material which Professor Bauer calls non-copper steel really contains, according to his own statement, about 0.10 percent copper. Professor Bauer has, therefore, not compared copper steel with non-copper steel, but has compared two copper steels, one with the other. In a paper which I read before the 1919 meeting of the American Society for Testing Materials, I showed that 0.10 percent copper is almost sufficient to give the maximum corrosion resistance to the average open-hearth and bessemer steel, even when the sulphur content is as high as 0.07 or 0.08 percent.

O. W. Storey[9] (*Communicated*): The data presented in this paper are very interesting and show what may result when steels are subjected to special and unusual conditions. These special tests are of interest in themselves as such, and great care must be used in applying these results to any other conditions, as it has been repeatedly shown that each corrosion problem must be solved by itself. While copper steel may be corroded much more rapidly by strong aluminum sulphate solutions than "pure iron," the corrosion of both is evidently rapid enough to require the use of some other metal in contact with such solutions. Where the iron or steel is corroded rapidly, I believe that tests are of little commercial value in view of the futility of trying to use apparatus which would in any case be rapidly corroded by the chemicals which are in contact with it.

The authors point out that copper steel is only resistant to special atmospheric conditions such as are obtained in Pittsburgh. They ignore entirely the results obtained by the American Society for Testing Materials at Fort Sheridan, where a comparatively

[9] Metallurgical Engineer, c/o C. F. Burgess Labs., Madison, Wis.

pure atmosphere is checking the Pittsburgh tests closely. My own data collected from corroded fence wire also show that copper steel is much more resistant to corrosion both in an acid atmosphere and in a comparatively pure atmosphere.

The authors quote Professor O. Bauer's work in Germany to substantiate the claim that copper steels are only of benefit in an acid-bearing atmosphere. A study of Professor Bauer's work shows that in an acid-bearing atmosphere an increase of copper content is of benefit, whereas in a neutral atmosphere 0.10 percent copper gives as much protection as a higher copper content. In an acid-bearing atmosphere his results check up my data obtained in the corrosion of copper steels in stoves, and it is evident therefore that where an atmosphere contains a high percentage of corroding agents a higher copper content is apparently of benefit. There is a limitation to the content of corroding agents which may be present in the atmosphere above which all ordinary steels apparently corrode alike. This is shown in my discussion of the paper by Aupperle and Strickland. (Trans, Am. Electrochem. Society, 1921, **39**, 136).

J. Newton Friend[10] (*Communicated*): At first sight it would appear very remarkable that such widely divergent views could be held by different authorities as to the influence of alloyed copper upon the corrodibility of iron. Nickel, which in many of its chemical properties closely resembles copper and stands very near to it in the Periodic Table of the Elements, is well known to retard corrosion, provided it is present in amounts ranging from not less than about 3 percent upwards. Cobalt appears to act somewhat similarly,[11] and as it is the congener of nickel in the Periodic Table, standing next to it on the side of lower atomic weights, it seems not unreasonable to suppose that if alloyed copper should have any influence upon corrosion, it should be in the direction of reducing corrosion.

Analogy in these cases is not a safe guide. The only satisfactory conclusions are those based upon a critical study of the results of practical investigation.

The earliest workers in this field appear to have regarded cupri-

[10] Municipal Technical School, Birmingham, Eng.

[11] See the experiments of Burgess and Aston, Eighth Inter. Cong. Applied Chem., 1912. Blake, Iron Age, 1917, **99**, 201.

ferrous iron as more highly resistant to corrosion than the ordinary metal[12] and this is quite in accordance with the results of Williams [13], Stead and Wigham[14], and the recent classical researches of Buck[15] (to mention only a few of the more important) in both acid and neutral media. It is distinctly disconcerting to find, therefore, that such an eminent authority as Dr. Cushman should be led to conclude, as the result of his own experiments, that copper is not a desirable metal to have admixed with iron. Dr. Cushman and his colleague, Mr. Coggeshall, mention on page 97 that their "tests were made in good faith,[16] and in order to gain such information as it was possible to obtain under the simple conditions of quiescent immersion" of their samples. They very candidly point out that their results do not agree with those of Richardson, published in 1920, and are, moreover, in direct contradiction to those of Bell and Patrick published in March of this year. Nor is this to be wondered at, for a casual glance at the analyses of the metals, as given on pages 86, shows that the three steels employed are not comparable. The metal Cb may be at once ruled out, for, while it contains some six times as much copper as Ab, it also possesses nearly nine times as much arsenic as Ab, and until the influence of arsenic upon corrodibility has been determined it is hardly logical to attribute any observed differences to the copper. Again, metal Kb contains some twenty times as much manganese as Ab, but only five times as much copper. Now Sir Robert Hadfield and the present writer[17] have shown that the presence of small quantities of manganese enormously enhances the rate of solution of iron in dilute acid. The solutions employed by Dr. Cushman (page 93 *et seq.*) were virtually dilute acids in consequence of the hydrolysis of the dissolved aluminium sulphate, so that, apart from its copper content, an increased corrosion rate was to be expected in the case of Kb, in view of its higher manganese content. Similar remarks apply to the acid tests described on page 96. It is regrettable that such obviously unsuitable material should have been used in the experiments which have in other respects evidently been carried out with

[12] See Karsten, British Assoc. Reports, 1838, p. 265.
[13] Williams, Proc. Eng. Soc. West. Penna., 1900, **16**, 231.
[14] Stead and Wigham, J. Iron Steel Inst., 1901, **II**, 122.
[15] Buck, Jour. Ind. Eng. Chem., 1913, **5**, 452.
[16] This is taken for granted.
[17] Hadfield and Friend, J. Iron Steel Inst., 1916, **I**, 48.

considerable skill and precision. The results are clearly uncertain, and cannot be regarded as offering any evidence either in favor of, or against the view that the presence of alloyed copper tends to reduce the corrodibility of iron under these conditions.

Considered apart from the copper question, however, the experiments with aluminium sulphate solution are very suggestive and are of particular interest to the writer in view of his recent colloid theory of corrosion[18].

A. S. Cushman (*Communicated*): By an unfortunate printer's error which was not detected until long after the preprint of the article was distributed, the arsenic content of the Cb samples, as shown on page 86, was printed 0.102, which made it appear as though the Cb samples contained about nine times more arsenic than the samples of Kb and Ab. This misprint may have misled some critical readers of the paper and led to the conclusion that it was not fair to make comparisons between samples so widely different in arsenic content, in view of the fact that so little is known at present in regard to the influence of arsenic on corrosion resistance. As a matter of fact, the arsenic content of the Cb samples should have been printed 0.012, which was identical with the arsenic content of the Ab samples and practically identical with the arsenic content of the Kb samples.

[18] Friend, J. Chem. Soc., 1921, **119**.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

SOME OBSERVATIONS ON THE MECHANISM OF THE INCREASED CORROSION RESISTANCE OF STEEL AND IRON DUE TO SMALL COPPER CONTENTS.[1]

By D. M. Buck.[2]

By adding small amounts of copper (approximately two-tenths percent) to steel and iron, the corrosion rate, under conditions where the product is alternately wet and dry, is tremendously reduced, and even quite minute amounts of copper are appreciably effective. The reason for this phenomenon is not definitely known, although several tentative explanations and theories have been offered by various investigators. Dr. W. H. Walker[3] has suggested that "copper prevents the oxides of manganese and iron from separating out between the crystal grains." Burgess and Aston[4] have stated that "increased resistance to corrosion might be expected, since the solid solution of the two elements might decrease the solution tendency of the iron; or if the iron finally goes into solution it may leave a deposit of copper forming a film and protect the underlying metal from further attack." E. A. and L. T. Richardson[5] have offered what they term the film or inter-grain theory to explain the inhibitive effect of copper. The author in one of his earlier papers on this subject[6] has suggested that "the alloy of copper and iron is less electro-positive to the first film of rust formed than is non-copper steel, and the consequent decrease in difference of potential lessens the corrosion." Later work indicates a probable reaction between the sulphur and copper, which seems to counteract the harmful effect of sulphur, and also that the structural characteristics of the rust film itself have an important bearing on the subject. The latter influence may be either primary or secondary. Which, if any, of these theories is the true explanation is problematical, and it is the intention of this paper to offer some data which seem to strengthen the sulphur-control and rust-film theories, mentioned above, and

[1] Manuscript received February 4, 1921.
[2] Metallurgical Engineer, American Sheet and Tin Plate Co., Pittsburgh, Pa.
[3] For references see end of paper.

to stimulate, if possible, further discussion and research by other investigators probably better equipped than the author to solve this problem.

In a previous report[6] the author finds that by adding copper in varying amounts to a heat of steel carrying 0.031 percent sulphur, the maximum efficiency, from a corrosion standpoint, is reached at about 0.07 percent copper. In a similar set of experiments on a heat carrying 0.055 percent sulphur, the point of maximum efficiency is not reached until approximately 0.12 percent copper, and that the corrosion losses on sheets rolled from those ingots in which no copper had been added were nearly three times as great in the high sulphur as in the low sulphur heat.

Many investigators have noted and commented upon the remarkable difference between the dense, dark colored, and closely

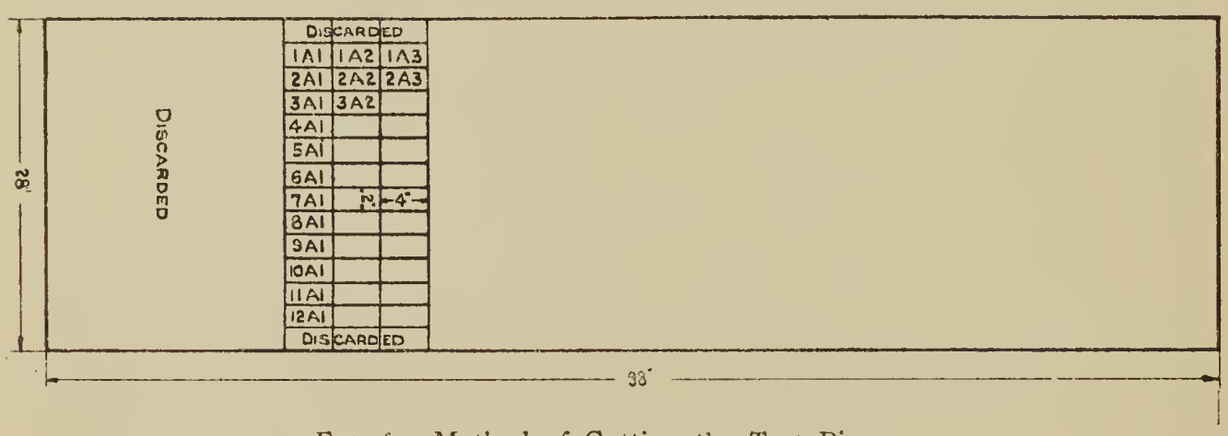


FIG. 1. Method of Cutting the Test Pieces.

adherent rust film on copper steel, and the loose, spongy and light red film on non-copper steels. It is apparent that the dense rust film which forms on copper steel becomes a real and fairly efficient protector to the underlying metal, and experiments have shown that the corrosion rate on copper steels becomes less after several months' exposure. In order to obtain data relative to this phase of the subject, the author is conducting a series of tests covering a period of four years' duration, and which have now been in progress for thirty-two months. For the reason that the results seem to bear on this phase of the subject under discussion, the author will offer at this time some tables and charts showing these results to date.

While pouring a heat of basic open-hearth steel, varying amounts of copper were added to the ingots and subsequent bars from each ingot were rolled into 16 gauge (1.6 mm.) sheets. Two

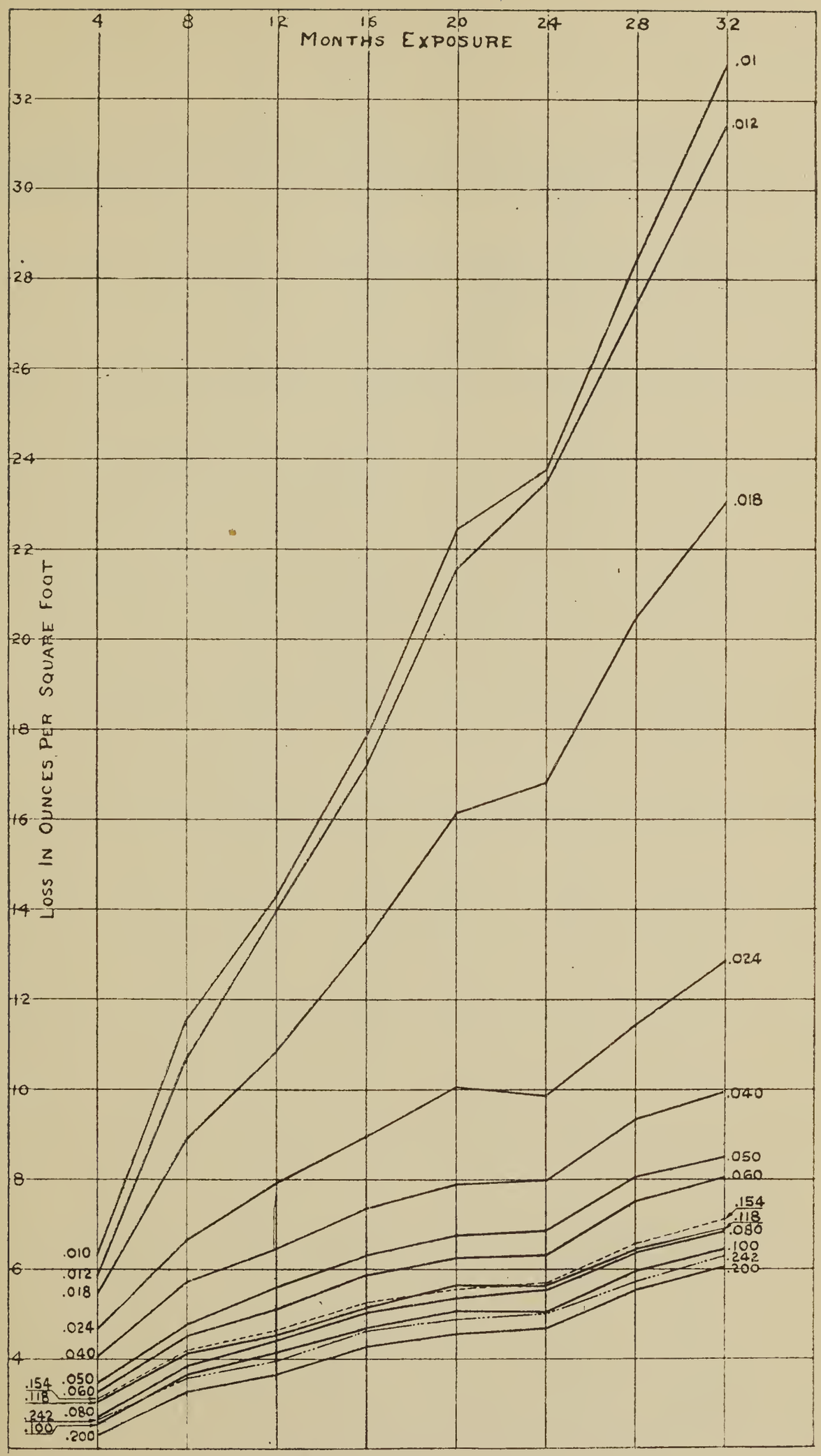


Fig. 2. Losses on Specimens Cleaned with Citrate.

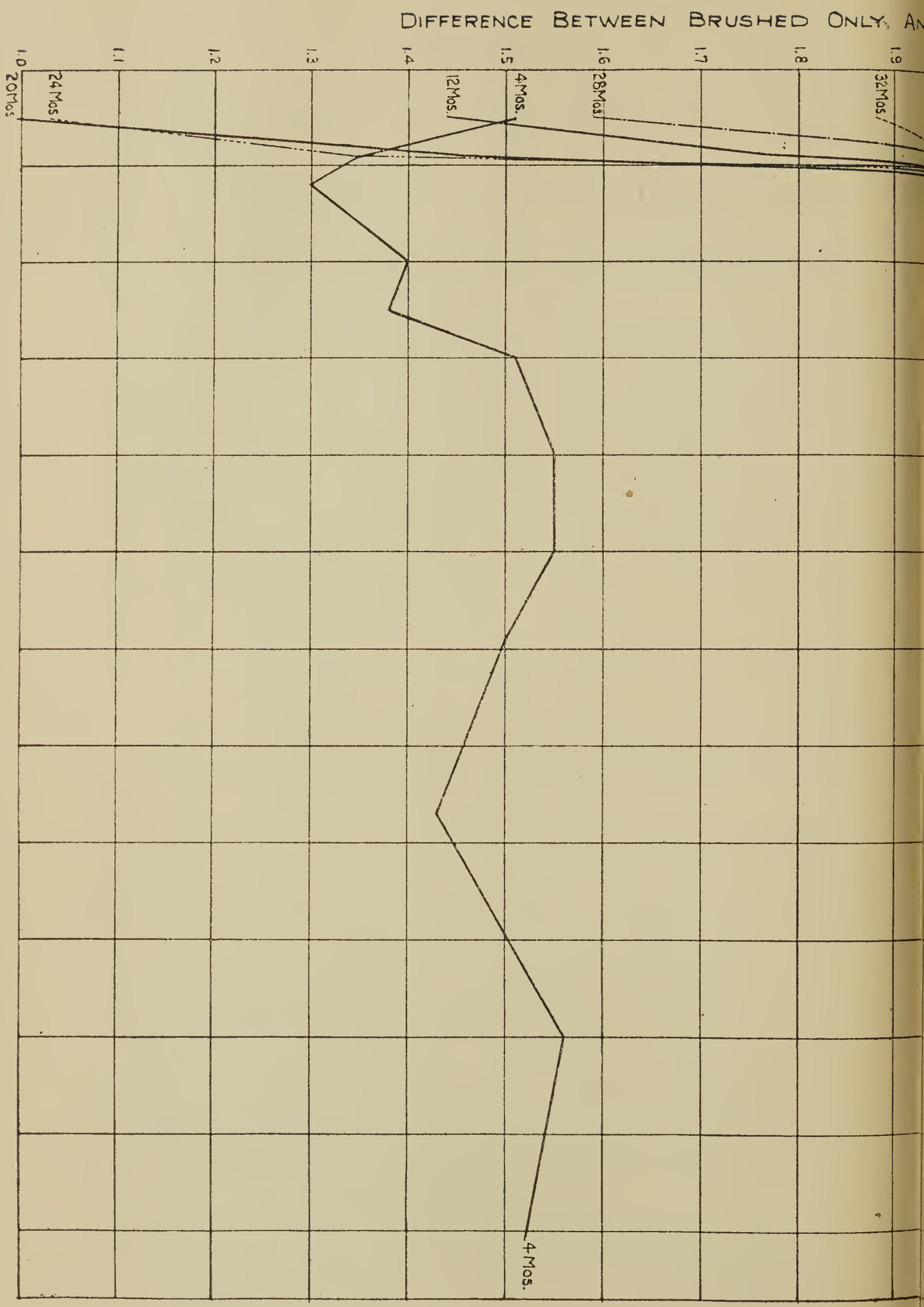
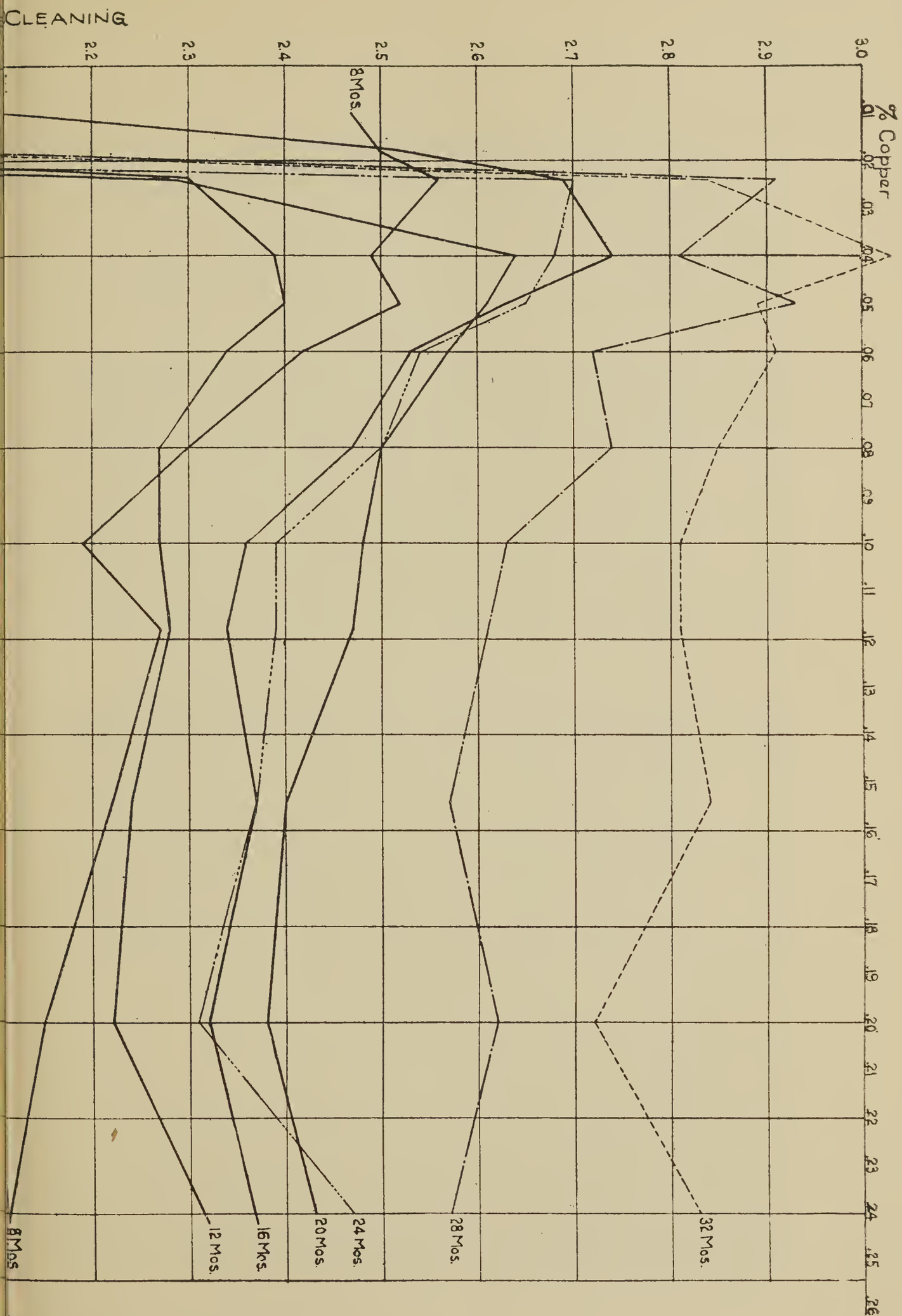


FIG. 3. Amount of Scale Remaining Aft



ire Brush at Various Copper Contents.

TABLE 1.

Losses in Ounces per Square Foot.
Each result is the average of six test specimens.

Symbol	Percent Copper	Months Exposure							
		4	8	12	16	20	24	28	32
		Brushed Only.							
A-B.....	0.010	4.81	9.11	12.85	15.73	21.48	22.73	26.86	30.90
C-D.....	0.018	4.07	6.41	9.05	10.82	14.63	15.46	18.46	21.04
E-F.....	0.024	3.30	4.11	5.63	6.28	7.76	7.15	8.51	9.99
G-H.....	0.040	2.62	3.23	4.08	4.62	5.24	5.31	6.51	6.94
I-J.....	0.050	2.09	2.27	3.20	3.69	4.17	4.19	5.11	5.61
K-L.....	0.060	1.76	2.11	2.76	3.35	3.69	3.78	4.79	5.10
M-N....	0.080	1.17	1.54	2.13	2.55	2.87	3.03	3.65	3.99
O-P.....	0.100	1.03	1.45	1.88	2.33	2.58	2.63	3.34	3.62
Q-R.....	0.118	1.56	1.86	2.27	2.81	3.14	3.23	3.83	4.06
S-T.....	0.154	1.67	1.98	2.38	2.88	3.15	3.26	4.02	4.27
U-V.....	0.200	.76	1.15	1.43	1.96	2.17	2.35	2.93	3.33
W-X....	0.242	1.08	1.48	1.64	2.24	2.46	2.54	3.16	3.47
Y-Z.....	0.012	4.37	8.48	12.34	14.86	20.49	22.22	25.87	29.80
		Cleaned with Citrate.							
A-B.....	0.010	6.32	11.58	14.29	17.83	22.43	23.76	28.45	32.78
C-D.....	0.018	5.42	8.91	10.82	13.34	16.08	16.80	20.47	23.04
E-F.....	0.024	4.66	6.67	7.93	8.97	10.05	9.85	11.42	12.83
G-H.....	0.040	4.02	5.72	6.47	7.36	7.88	7.99	9.33	9.97
I-J.....	0.050	3.47	4.79	5.60	6.32	6.78	6.84	8.04	8.50
K-L.....	0.060	3.27	4.53	5.10	5.88	6.26	6.32	7.51	8.01
M-N.....	0.080	2.72	3.84	4.40	5.02	5.37	5.53	6.39	6.84
O-P.....	0.100	2.58	3.64	4.15	4.69	5.06	5.02	5.97	6.43
Q-R.....	0.118	3.06	4.13	4.55	5.15	5.61	5.62	6.44	6.87
S-T.....	0.154	3.10	4.20	4.62	5.25	5.55	5.63	6.59	7.11
U-V.....	0.200	2.32	3.30	3.65	4.28	4.55	4.66	5.55	6.05
W-X....	0.242	2.60	3.59	3.96	4.61	4.89	5.01	5.73	6.30
Y-Z.....	0.012	5.83	10.68	14.00	17.21	21.58	23.49	27.46	31.44

sheets from each ingot, 16 gauge, 28 x 96 inch (70 x 240 cm.) were used for the test. Two inch (5 cm.) wide strips were discarded from one side and twenty inches (50 cm.) discarded from one end of each sheet. Three strips, each four inches (10 cm.) wide, were then sheared from across each sheet, and each strip cut into 2 x 4 inch (5 x 10 cm.) test specimens. Each piece was carefully marked, designating its position in the sheet. Fig. 1 will give an idea of the procedure in cutting these 2 x 4 inch pieces. The test pieces were then cleaned, carefully weighed, and mounted in

twelve wooden racks, each being an exact duplicate of the other. Rack No. 1 thus contained all of the samples marked No. 1, rack No. 2 all of the samples marked No. 2, etc. Since two sheets of each grade were used, the results recorded are the averages of six samples from each grade. The racks containing the test specimens were exposed to the weather at Scottdale, Pa., and were removed, in order, after periods of four, eight, twelve, and sixteen months, etc. The test pieces from each rack, after it was removed from the test, were carefully brushed with a stiff wire brush to remove all of the rust which was not closely adherent. The pieces were then carefully weighed and the remaining rust removed by an ammoniacal solution of ammonium citrate, and the test pieces again weighed.

Table I gives the losses in weight for each individual rack up to and including thirty-two months' exposure, and Fig. 2 expresses these results graphically.

Table II has been obtained by subtracting the results obtained from the samples which were brushed only from those which were cleaned with citrate, the figures thus representing the amount of rust film which was closely adherent and not removed by wire brushing. A small iron loss is incident to cleaning with citrate, but experiments have shown it to be quite small and approximately the same on all grades of steel and iron.

Although it is recognized that cleaning with wire brush is not an exact method, yet care was taken to treat all pieces as nearly alike as possible, and the averages on such a large number of samples should be fairly indicative.

An examination of the results shows that, in general, the rust film on the higher copper steels is more adherent and thicker than on those grades containing lower copper contents, and also that, as the time element increases, the protective rust film also increases. A dry season is reflected in the period from 20 to 24 months.

Fig. 3 is a graphic representation of Table II.

From the data at hand it seems there is a strong indication that the well-known harmful influence of sulphur on corrosion is in some manner controlled by the addition of copper, and also that the structure of the rust film formed is a function of the increased resistance peculiar to copper steel. This difference in structure

TABLE II.

Amount of Scale Remaining After Cleaning with Wire Brush. Ounces per Square Foot.

Symbol	Percent Copper	Months Exposure							
		4	8	12	16	20	24	28	32
		Differences.							
A-B.....	0.010	1.51	2.47	1.44	2.10	0.95	1.03	1.59	1.88
C-D.....	0.018	1.35	2.50	1.77	2.52	1.45	1.34	2.01	2.00
E-F.....	0.024	1.30	2.56	2.30	2 69	2.29	2.70	2.91	2.84
G-H.....	0.040	1.40	2.49	2.39	2.74	2.64	2.68	2.81	3.03
I-J.....	0.050	1.38	2.52	2.40	2.63	2.61	2.65	2.93	2.89
K-L.....	0.060	1.51	2.42	2.34	2.53	2.57	2.54	2.72	2.91
M-N....	0.080	1.55	2.30	2.27	2.47	2.50	2.50	2.74	2.85
O-P.....	0.100	1.55	2.19	2.27	2.36	2.48	2.39	2.63	2 81
Q-R.....	0.118	1.50	2 27	2.28	2.34	2.47	2.39	2.61	2 81
S-T.....	0.154	1.43	2.22	2.24	2.37	2.40	2.37	2.57	2.84
U-V.....	0.200	1.56	2.15	2.22	2.32	2.38	2.31	2.62	2.72
W-X....	0.242	1.52	2.11	2.32	2.37	2.43	2.47	2.57	2.83
Y-Z.....	0.012	1.46	2 20	1.66	2.35	1.09	1.27	1.59	1 64

may be due to the slower corrosion rate, and it also seems probable that, at a later period, it acts mechanically as a protector of the underlying metal. It also seems probable that the theory of sulphur control, above mentioned, does not completely explain the phenomenon, for the reason that Burgess and Aston[4] find that by adding copper to pure electrolytic iron (presumably sulphurless), beneficial results are obtained from a corrosion standpoint. The true explanation may lie in a combination of two or more of the various theories that have been advanced.

The writer sincerely hopes that this very interesting subject will be given attention by students of corrosion as the finding therefrom may lead to still further advancement in the inhibition of corrosion.

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5. E. A. and L. T. Richardson, "The Influence of Copper, Manganese and Chromium and Some of Their Combinations on the Corrosion of Iron and Steel," Trans. American Electrochem. Soc. (1920), **38,** 221.
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DISCUSSION.

G. W. GOGGESHALL[1]: I notice that Mr. Buck says, on page 110, that experiments have shown that the corrosion rate on copper steels becomes less after several months' exposure. This confirms what Mr. Buck has previously announced. In 1917, in the Transactions of the American Electrochemical Society, Mr. Buck, in the discussion of Mr. Storey's paper on the Corrosion of Fence Wire (**32**, 314, of the Transactions) states: "Mr. Storey has mentioned the influence of the rust film on the corroded wire. The peculiarity about copper steel is that after approximately 12 months' exposure rusting action, due to the formation of the protective film, nearly, if not completely, stops. I have demonstrated this fact by observations on many full-sized corrugated sheets and also by weight—by exposing large numbers of small test pieces and taking down and re-weighing at regular intervals a certain number of each grade. Normal steel continues to lose weight until complete destruction, the corrosion rate increasing toward the end of the period; whereas in the case of copper steel, after 10 or 12 months' exposure, corrosion practically ceases, a dense, almost vitreous, coating being formed on the surface." In his present paper Mr. Buck gives the average losses of six test specimens which were exposed to the atmosphere, and he shows that the copper bearing steel continues to corrode instead of ceasing corrosion. In Fig. 2 is graphically shown the extent of the corrosion of all the forms of steel with the various amounts of copper in them, and it shows that the copper bearing steel in 32 months lost about 1.6 times as much as it did in 12 months, while the extremely low copper samples lost 2.2 times as much in 32 months as they did in 12 months. In fact, Fig. 2 shows that the total corrosion on copper steel is almost linear with the time in months. These lower lines in Fig. 2 are almost a straight line. There apparently was as much loss between 24 and 32 months as there was between 4 and 12 months.

There is one other point I would like to inquire about. Mr. Buck used No. 12 gauge (2.77 mm.) sheets. They weigh about 40 ounces per square foot. In his table, on page 114, he gives losses

[1] Chemical Engr., The Institute of Industrial Research, Washington, D. C.

in ounces per square foot. Some of these losses reach as high as 31 or 32 ounces. I am not sure whether he means losses per square foot of surface or losses per square foot of metal. One is double the other, of course.

D. M. Buck: The losses are expressed in ounces per square foot of metal. I think that my statement several years ago was that the corrosion after twelve to fifteen months nearly, if not completely, stops. Later information, including data up to 32 months' total exposure, indicate that, although the corrosion does not completely stop, yet the rate of corrosion on the copper steels is remarkably slow when compared with non-copper steels. The loss on copper steels during the period between 8 months' exposure and 32 months' exposure has been only a little more than two ounces per square foot (0.6 kg. per sq. m.). In the same period the non-copper steels have shown a loss of about 21 ounces per square foot (6.4 kg. per sq. m.).

G. W. Coggeshall: My point was not the relative rates of corrosion, but was simply that the corrosion did not stop, and I still cannot see but that the corrosion continues at practically the same rate between the first and second years as it does in the first year, although apparently at a less rate than with other classes of metal, but that was not the point I was bringing out.

L. T. Richardson[2]: In this very interesting paper on the corrosion of iron or steel containing copper, Mr. Buck has thrown light upon some of the factors that are responsible for the increased corrosion resistance of steels containing copper. This is discussed from the viewpoint of two factors, namely, the control of the harmful effects of sulphur, through the influence of copper, and the protective action of a layer of closely adhering rust. A previous paper by Mr. Buck gives evidence of the effect of sulphur control; the present paper deals with evidence that shows the influence of the rust film or layer. It is also stated that other factors may have a great influence, and partially explain the rust resistance of copper bearing steel, such as an increased resistance to corrosion of the metal itself.

Attention is called to the closely adhering rust which forms on copper steel, which fact has been noticed and mentioned by other

[2] Chemical Engineer, Cutler-Hammer Mfg. Co, New York City.

observers, who also have commented upon the probably positive effect that it might have in decreasing corrosion. I believe with these other observers that the rust film decreases corrosion, in fact, I do not see how it could be otherwise, since a closely adhering layer must hinder the corroding media from reaching the underlying iron surface. The question is one of the relative importance of these various factors. Personally I do not believe that it is of as much importance as some of the other factors, for the very existence of an adherent layer must be partially due directly or indirectly to the changed composition of the iron.

There are some interesting interpretations of Mr. Buck's data, which tend to throw light upon this question.

In considering the effect of the rust layer on corrosion, it eliminates one source of error if deductions are made after the surface of the iron has reached, or approximately reached, some state of equilibrium, since a large number of other interfering factors are exerting an influence during the early stages of corrosion. From the data in Table I, and particularly the graphs in Fig. 2, this state appears to be reached at about eight months, and thereafter rusting proceeds at a fairly uniform rate. If in Fig. 2 for any given composition, a straight line is drawn connecting the points representing the corrosion at 8 months, and at 32 months, it will be found that the observed values correspond within experimental error to the values determined from the straight line.

If one considers the graphs in Fig. 3, which show the amount of adhering rust at different times for various additions of copper, one notes that after a certain small percentage of copper has been added the quantity of adhering rust does not increase, but actually decreases a small amount. It seems that beyond a certain content the amount of adhering rust is practically independent of the alloyed copper. Fig. 2, however, indicates that the copper content has a great influence on the amount of corrosion. To illustrate, take the graph in Fig. 3 representing the adhering rust at 28 months. After 0.024 percent copper and up to 0.242 percent copper the amount of adhering rust is not increased by increase of copper content. From Fig. 2, however, it is seen that the actual loss by corrosion has been reduced one-half, from 11.42 oz. per

sq. ft. in the case of 0.024 percent copper to 5.73 oz. per sq. ft. in the case of 0.242 percent copper.

The graphs giving the amount of adhering rust also show, as Mr. Buck has pointed out, that the quantity of rust increases with the copper content. Beyond about 0.04 percent copper the quantity of adhering rust is almost directly proportional to the amount of corrosion, for equal times.

When all these factors are taken into account, that after a certain time the rate of corrosion is constant, that after a certain percentage of copper (about 0.05 percent) the amount of adhering rust formed during a given period of time is practically independent of the copper content, and that after about 0.05 percent copper the adhering rust is directly proportional to the total corrosion, one is led to the belief that other factors besides the protecting action of the rust are exerting a very pronounced influence on the corrosion. The amount of adhering rust, as well as the amount of total rust, is a measure of the total amount of corrosion. The rate of corrosion appears to be influenced by the composition of the metal surface exposed.

E. A. Richardson[3] (*Communicated*): Mr. Buck's paper and especially his graphs are very instructive and interesting.

The curves in Fig. 2 show that after the initial rapid corrosion for the first 8 months, which occurs in all steels regardless of copper content, the corrosion rate for each steel becomes constant and does not decrease, at least in 32 months. It is possible that the rapid initial rate may have been due to weather conditions in which event the rate of corrosion would have been fairly uniform over the entire period.

These curves also show that the rate of corrosion after rust has formed is no greater than the initial rate. This would seem to be contrary to the idea, often expressed but not proved that the presence of rust stimulates corrosion.

It seems to me that the curves show that the dominant factor in the decreased corrosion of copper bearing steels is the composition of the metal itself, and that the adherence of the rust coating is a secondary factor.

[3] Chemist, National Lamp Works of General Electric Co., Cleveland, Ohio.

O. W. Storey[4] (*Communicated*): The function of copper in preventing excessive corrosion of iron and steel has not been satisfactorily explained up to the present time. This paper shows progress in explaining the function of the copper. It is evident from this work and from work previously reported by Mr. Buck that sulphur causes excessive corrosion and that copper counteracts this deleterious influence. Mr. Buck also points out in this paper the value of the mechanical protection of the rust. This mechanical protection has been observed in many cases, but this paper shows the numerical relationship of this protection.

While I believe that the copper protects the steel primarily by counteracting the corrosive effect of sulphur as pointed out by Mr. Buck, I believe that there are secondary effects which are also important. I have reference especially to the element phosphorus. In studying the last report of the corrosion committee of the American Society for Testing Materials, I noted that, while some 22-gauge copper steel sheets had not failed, other 22-gauge steel sheets containing equal quantities of copper had failed. In making a close study of the analyses furnished, it appears that the steels made by the acid process which were high in phosphorus were much more resistant to corrosion than the steels made by the basic process, which were low in phosphorus. None of the other elements apparently had any influence. While phosphorus has been shown by Mr. Buck to have a favorable influence on the corrosion of steel, it may be possible that when in combination with copper it has a secondary effect which intensifies the action of the copper. While this hypothesis is based only on the meager data available, as presented in the last report of the Corrosion Committee of the American Society for Testing Materials, it is apparent that there is a decided difference between the basic and acid open-hearth copper steels to which copper has been added. As the corrosion of the American Society for Testing Materials' sheets proceeds, the influence of the phosphorus will become more or less apparent, and it may be possible that definite conclusions may be reached in the matter. It may be possible that the addition of phosphorus to some of the pure irons or low phosphorus basic open-hearth steels will have a favor-

[4] Metallurgical Engineer, C. F. Burgess Labs., Madison, Wis.

able influence and make them as resistant to corrosion as the acid open-hearth or Bessemer-copper steels are at present.

In looking over a large number of analyses on fence wires, with and without copper, it was found impossible to draw any conclusions from these analyses, as in most cases the phosphorus content was high, and in those cases where the phosphorus content was low it was impossible to draw any conclusions because of other conditions. It is apparent, then, that the influence of phosphorus in connection with copper will have to be made a subject of further research, should the results from the corrosion tests of the American Society for Testing Materials warrant it.

The objection may be raised that wrought iron contains a high percentage of phosphorus and that the wrought iron sheets containing copper in the corrosion tests of the American Society for Testing Materials failed in a comparatively short time. I believe that it is not possible to apply the results of the corrosion tests with steel directly to those of wrought iron because two entirely different materials are being considered.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

OBSERVATIONS ON THE CORROSION OF IRON AND STEEL.[1]

By J. A. Aupperle[2] and D. M. Strickland.[3]

Abstract.

A record of tests on pure iron* made in open-hearth furnaces, copper iron, plain steel and copper steel, to determine their resistance to a continuation of ferrous, ferric sulphate and sulphuric acid corrosion. The specimen sheets were tested 60 days in each case, either alone or fastened to sheets of pure iron by copper rivets or iron rivets, forming galvanic couples. In all the cases cited pure iron made in open-hearth furnaces had the smallest corrosion losses. [J. W. R.]

During the past few years many articles have been written concerning the rate of corrosion of bare copper-bearing iron and steel sheets when exposed to atmospheric conditions. It is a well-known fact that materials behave differently when tested under different conditions, and that an atmospheric test on sheet metal is no criterion whatever as to the durability of the metal where water instead of air predominates. It has been our experience that some metals showing up well under one condition of exposure disintegrate badly when exposed under different conditions. When materials are exposed in the atmosphere the test conditions are as a rule highly oxidizing. The following tests were conducted under reducing conditions.

We decided to conduct practical immersion tests to determine the effect of copper from a corrosion standpoint. We chose for the corroding medium a solution containing 0.7 sulphuric acid, 1.98 ferrous sulphate and 0.15 percent ferric sulphate. We constructed a pure iron tank 12 x 18 x 30 inches (30 x 45 x 75 cm.)

[1] Manuscript received March 3, 1921.
[2] Chief Chemist, American Rolling Mill Co., Middletown, Ohio.
[3] American Rolling Mill Co., Middletown, Ohio.
* Where pure iron is referred to in this paper is meant commercially pure iron.

and assembled suitable equipment for circulating the electrolyte. The accompanying photograph (Fig. 1) shows the airlift employed. The globe valve regulates the air supply. The air blowing up the vertical pipe draws liquid through the short pipe from the bottom of the tank. We found that by this means it required but a very small amount of air to lift the acid mixture from the bottom of the tank to a pipe parallel to and above the V-shaped trough which was placed between this pipe and the surface of the liquid. The solution was kept circulating continuously and was thoroughly aerated.

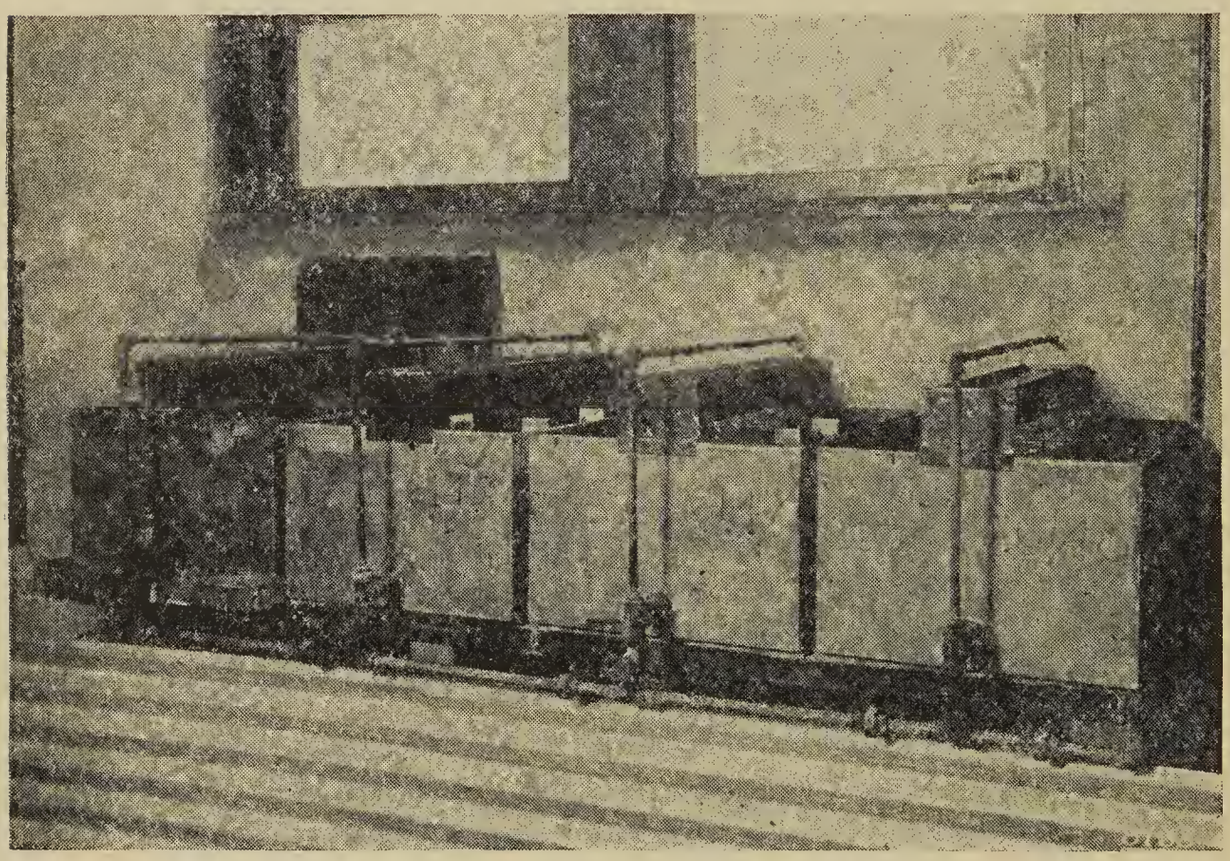

Fig. 1.

We conducted these tests on various grades of pickled iron and steel, No. 16 gauge (1.6 mm.), 6 x 6 inch (15 x 15 cm.) test pieces. These samples contained a half inch (1.3 cm.) hole and were suspended on a ⅜ inch (1 cm.) glass rod.

We tested the acid strength daily and found that in approximately 10 days the acid content had decreased from 0.7 to 0.04 percent, and that the ferrous sulphate had increased from 1.98 to 2.62 percent. We then fortified the solution with sufficient sulphuric acid to bring it back to the original 0.7 percent. We found that

in conducting this test there was considerable evaporation, and we maintained the volume of solution at a fixed level by the introduction of a sufficient amount of water each day to replace that which had evaporated.

We conducted this test at room temperature for 60 days. The results obtained in 60 days are given in Table I, which show considerable differences between the rates of corrosion of the various metals. The copper-bearing steel lost almost four times as much as pure iron.

TABLE I

Material	S	P	C	Mn	Cu
Pure iron	0.015	0.006	0.010	0.012	0.018
Copper iron	0.036	0.006	0.010	0.027	0.304
Plain steel	0.035	0.006	0.100	0.570	0.042
Copper steel	0.035	0.006	0.100	0.470	0.340

Material	Loss in 60 Days	
	Oz. per Sq. Ft.	Grams per Sq. Meter
Pure iron	0.380	118
Copper iron	0.430	134
Plain steel	0.832	259
Copper steel	1.213	378

We also conducted tests on other materials, duplicates of which had been previously exposed in atmospheric tests for many months. Table II shows results that were obtained on No. 16 gauge (1.6 mm.), 2 x 6 inch (5 x 15 cm.) pickled samples after 60 days' immersion in the same corroding medium as above described and under the same conditions as the first test.

The results obtained in this test substantiate our belief that metals which resist the atmosphere for several years, subsequently lose several times as much weight in the immersion test as some of the materials which failed first in the atmospheric test.

Having obtained data showing that copper is harmful when added to steel when such steel is subjected to the action of the solution under consideration, we conceived the idea of riveting samples of various kinds of metal together.

TABLE II.

Material	S	P	C	Mn	Cu
Pure iron	0.026	0.003	0.013	0.024	0.021
Copper - bearing open - hearth steel	0.026	0.010	0.080	0.356	0.257
Open-hearth steel	0.045	0.012	0.063	0.411	0.075
Bessemer steel (coppered)	0.069	0.094	0.052	0.370	0.224
Copper acid open hearth steel	0.043	0.083	0.091	0.397	0.209
Bessemer steel	0.040	0.083	0.027	0.390	0.012
Puddled iron	0.022	0.057	0.036	0.030	0.307

Material	Loss in 60 Days	
	Oz. per Sq. Ft.	Grams per Sq. Meter
Pure iron	0.622	194
Copper-bearing open-hearth steel	0.750	233
Open-hearth steel	0.779	243
Bessemer steel (coppered)	2.060	641
Copper acid open-hearth steel	3.263	1016
Bessemer steel	Failed	Failed
Puddled iron	Failed	Failed

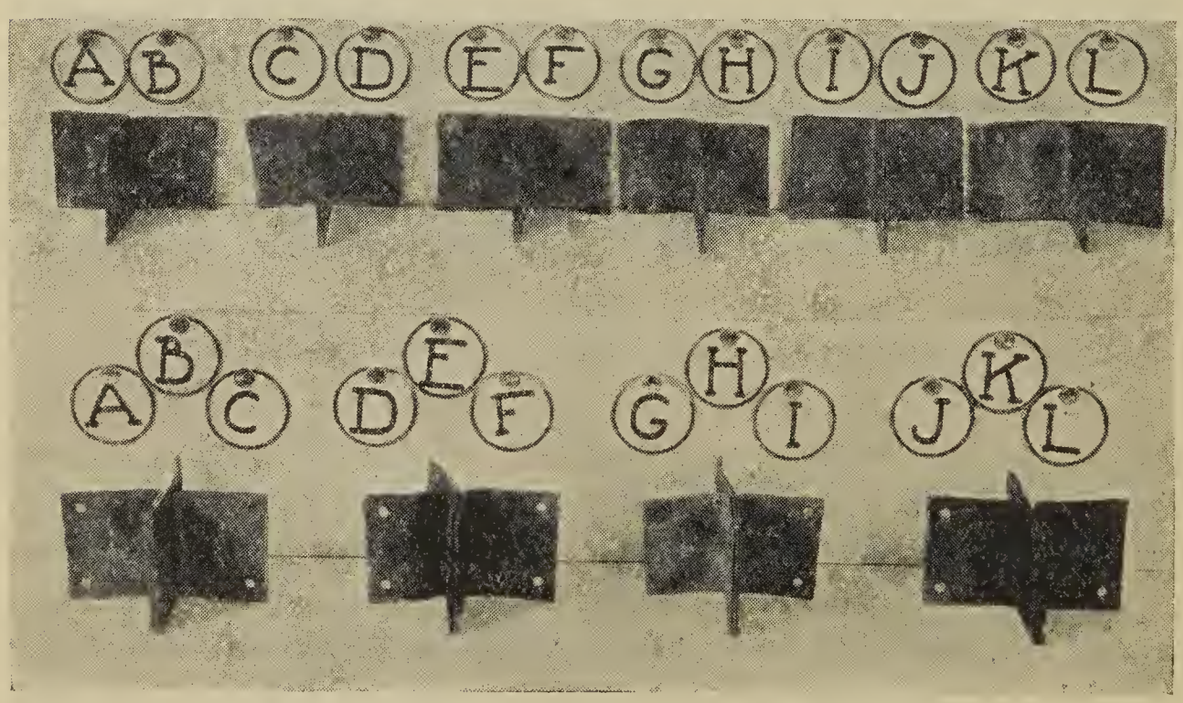

FIG. 2.

Samples of competing metals No. 16 gauge (1.6 mm.), 2 x 3 inch (5 x 7.5 cm.) material were selected for the rivet test. Small holes were drilled in the corners of the pieces used. The samples were then pickled and weighed. Different combinations of the various grades were riveted together in groups of two and three, using copper rivets in the four drilled corners. The metals were separated by the use of thin copper washers. The samples so prepared were placed in the same solution as above described, and very interesting results were obtained.

The accompanying photograph (Fig. 2) shows the corroded condition of several test pieces and the method of holding the various samples in contact with each other. The upper group of test pieces show typical examples of various pairs examined. The letters refer to the grade and are as follows:

A	Pure iron	G	Copper steel
B	Copper steel	H	Copper steel
C	Plain steel	I	Pure iron
D	Copper iron	J	Pure iron
E	Copper iron	K	Copper iron
F	Copper steel	L	Pure iron

The lower view of test pieces illustrates the groups of three and are described as follows:

A	Copper iron	G	Copper steel
B	Pure iron	H	Pure iron
C	Plain steel	I	Copper iron
D	Pure iron	J	Copper iron
E	Copper steel	K	Copper steel
F	Pure iron	L	Copper iron

The marked difference between such specimens as *D, F* and *H*, when compared with *E, G* and *K,* in the groups of three, and *A* and *J* compared with *B* and *C* in groups of two, show the condition of the samples when removed from the corroding liquid. With the exception of a few mechanical marks caused by tools in opening the samples, the surfaces of the pure iron samples were free from scars, while the copper steel samples were not only very thin but had rough surfaces and also showed very deep pitting where the washers and rivets touched the test piece.

Table III shows the average analysis, number of pieces used, and the average grade weight loss in 60 days.

We were very much surprised to know that copper could be used in direct contact with pure iron without material effect from a corrosion standpoint when the metals are used where liquids instead of air predominate. We have not yet concluded atmospheric tests where metallic copper is in contact with pure iron, and therefore wish to draw no conclusions at this time as to what would occur if air instead of water predominates.

TABLE III.

No. 16 gauge, 2 x 3 inch (5 x 7.5 cm.) Black, Pickled Samples, Copper Riveted.

Material	S	P	C	Mn	Cu	No. of Pieces Tested
Pure iron	0.025	0.005	0.012	0.018	0.028	11
Copper iron	0.028	0.006	0.010	0.015	0.204	12
Plain steel	0.020	0.012	0.090	0.273	0.034	10
Copper steel	0.025	0.011	0.110	0.420	0.235	14

Material	Av. Loss in 60 Days	
	Oz. per Sq. Ft.	Grams per Sq. Meter
Pure iron	0.51	159
Copper iron	0.51	159
Plain steel	1.18	367
Copper steel	3.40	1058

It is a well-known fact that copper is electro-positive to iron, and we expected that contact copper would have considerable effect upon all the grades of iron and steel.* The accompanying photograph (Fig. 2) shows that this is not so. The copper-bearing steel has been acted upon to a much greater extent than iron or copper-bearing iron. It is possible that the increased rate of corrosion of the copper-bearing steel was due to the presence of electro-negative manganese which changed the electro-potential of the steel, rendering it electro-negative to the iron.

Having obtained very interesting results as to the effect of

* In accordance with the custom of this Society, the metals acting as anodes in an electrochemical system are called electro-negative.

contact copper on the various metals, we decided to amplify the tests still further, and did so by riveting samples of dissimilar metals together with iron rivets instead of metallic copper, thus obtaining corrosion results from metals in contact which may have a difference of electrical potential. In other words, we will show not only the effect of contact copper, but also the effect of such potential difference as may exist and become effective when copper-bearing steel and iron are coupled in pairs with pure iron and immersed in the electrolyte.

The iron-riveted samples, in separate beakers, were immersed in the acidulated ferrous-ferric solution and kept at a temperature of 100° F. (38° C.) for ten days. No washers were used in this test, and we used No. 16 gauge (1.6 mm.), 2 x 3 inch (5 x 7.5 cm.) black pickled specimens of pure iron, copper iron and copper steel.

TABLE IV.

No. 16 gauge (1.6 mm.), 2 x 3 inch (5 x 7.5 cm.), Black, Pickled Samples, Iron Riveted.

Material	S	P	C	Mn	Cu	No. of Pieces Tested
Pure iron	0.025	0.005	0.012	0.018	0.028	15
Copper iron	0.029	0.007	0.011	0.021	0.268	14
Copper steel	0.025	0.011	0.110	0.420	0.235	14

Material	Av. Loss in 60 Days	
	Oz. per Sq. Ft.	Grams per Sq. Meter
Pure iron	1.93	601
Copper iron	2.40	747
Copper steel	7.78	2422

We noticed that some of the metals exhausted the acid supply more rapidly than others. When this point was reached, the slight oxidation to ferric iron tinged the solutions a brown color. Just as soon as this occurred the solution was again fortified with sufficient sulphuric acid to bring the strength up to 0.7 percent.

During the immersion of the iron-riveted samples it was noticed that the action was much more violent around certain grades

of material than others. This was indicated by the very rapid evolution of gases from certain test pieces, regardless of whether they were in the center or on the outside of the riveted groups of three. At the completion of the test an examination of the samples followed, and as was to be expected, the specimens which had shown the most violent action when in the corroding medium also suffered the greatest weight losses. It was also noted that many of the samples when removed from the solution had a reddish copper tinge.

Table IV covers the average analysis of the pieces used, together with the number employed in the test, and the loss in weight per 10 days.

The physical condition of the samples, after the test, was the same as the copper-riveted samples illustrated in Fig. 2. The copper-bearing steel pieces were quite thin and very rough. The copper iron samples were somewhat pitted, whereas the pure iron specimens were smooth in every instance. A comparison of weight losses shows that the copper-bearing steel again lost approximately four times as much weight as the pure iron.

In order to determine whether the presence of a small amount of copper was alone responsible for the rapid corrosion of any particular grade of material, we decided to again repeat the test, using samples which were alike except for the copper content. The copper iron used was obtained by adding copper to part of the melt from which the pure iron samples were taken. The copper steel was obtained in a like manner by adding copper to a portion of the plain steel melt. We then had at hand samples which were alike in analysis except for the copper content. Samples of 16 gauge (1.6 mm.), 2 x 2 inch (5 x 5 cm.), were riveted together; in some instances using copper rivets and in other instances iron rivets.

These samples were immersed in the acid solution in separate beakers at 100° F. (38° C.) for 10 days. They were then removed and weighed, the data obtained being tabulated in Table V.

The physical appearance of the samples at the completion of the test conformed to the description as previously given for the 2 x 3 inch (5 x 7.5 cm.) test pieces.

The fact that the weight losses of the copper-bearing steel samples are again approximately four times that of the pure

iron samples, is not so significant as the discovery that in each and every instance the samples representing the copper-bearing portions of the heats lost appreciably more in ounces per square foot than their companion pieces to which no copper had been added.

TABLE V.

No. 16 gauge (1.6 mm.), 2 x 2 inch (5 x 5 cm.), Black, Pickled Samples, Copper Riveted.

Material	S	P	C	Mn	Cu	No. of Pieces Tested
Pure iron	0.036	0.006	0.010	0.015	0.025	5
Copper iron	0.036	0.006	0.010	0.021	0.304	5
Plain steel	0.035	0.006	0.100	0.540	0.042	5
Copper steel	0.035	0.006	0.100	0.500	0.340	5

Material	Av. Loss in 10 Days	
	Oz. per Sq. Ft.	Grams per Sq. Meter
Pure iron	1.33	414
Copper iron	3.02	943
Plain steel	4.69	1460
Copper steel	5.02	1563

No. 16 gauge (1.6 mm.), 2 x 2 inch (5 x 5 cm.), Black, Pickled Samples, Iron Riveted.

Material	S	P	C	Mn	Cu	No. of Pieces Tested
Pure iron	0.036	0.006	0.010	0.015	0.025	5
Copper iron	0.036	0.006	0.010	0.021	0.304	5
Plain steel	0.035	0.006	0.100	0.540	0.042	5
Copper steel	0.035	0.006	0.100	0.500	0.340	5

Material	Av. Loss in 10 Days	
	Oz. per Sq. Ft.	Grams per Sq. Meter
Pure iron	1.17	364
Copper iron	2.81	875
Plain steel	3.66	1139
Copper steel	5.87	1827

SUMMARY.

1. We have developed a simple test which permits aerating and circulating the corroding medium. Such a test more closely approximates actual service conditions than immersion tests in a still liquid.

2. The presence of copper in iron and steel is detrimental when such metals are subjected to immersion tests where acidulated solutions of ferrous and ferric sulphates come in contact with such metals.

3. Samples alike in analysis except for copper content made from the same heats for this investigation indicate that the copper was responsible for the more rapid corrosion of the copper-bearing samples. The copper was the only variable factor in the two grades of metal.

4. Metallic copper in contact with various kinds of iron and steel containing various percentages of copper had little effect upon the corrosion of any of the metals with the exception of the copper-bearing steel which was attacked in areas surrounding the contact copper. A test which will show the effect of metallic copper in contact with iron and steel is of considerable importance, as copper fittings are used in hot water tanks, radiators, etc., and copper thermostats are used in boilers.

5. Without replenishing the acid as consumed, there is no uniformity of test conditions when the tests are immersed in separate vessels, for it is obvious that the samples which dissolved rapidly would soon use up the acid and the action cease, allowing the samples which dissolved more slowly to finally exhaust the acid, thereby equalizing the corrosion losses.

6. Our method of testing simulates many actual service conditions where iron and steel are employed, such as in the construction of tanks, coal cars, ore cars, boilers, boats, tubes, cables, smokestacks, etc. This is especially true for equipment in smelters using pyritic ores. Our results have an important bearing on all construction work, cars, boats, etc., where copper-bearing steel is in contact with iron or steel free from copper. Ferrous sulphate is formed from the oxidation of pyrites transported in cars and boats made from iron and steel used to transport pyritic ores

or coal containing iron pyrites. Boiler water taken from rivers sometimes contains ferrous and ferric sulphates. Mine water also contains these constituents with rapid attack upon iron and steel used in mines.

7. When dissimilar metals are used for the construction of tanks, boilers, pipes, etc., and when such metals are in contact with water containing ferrous sulphate and sulphuric acid, the iron or steel containing the most copper will be the first to fail.

DISCUSSION.

Colin G. Fink[1]: As far as atmospheric corrosion is concerned, copper steel would seem to stand up very well; but as far as electrolytic corrosion is concerned, it fails. I should like

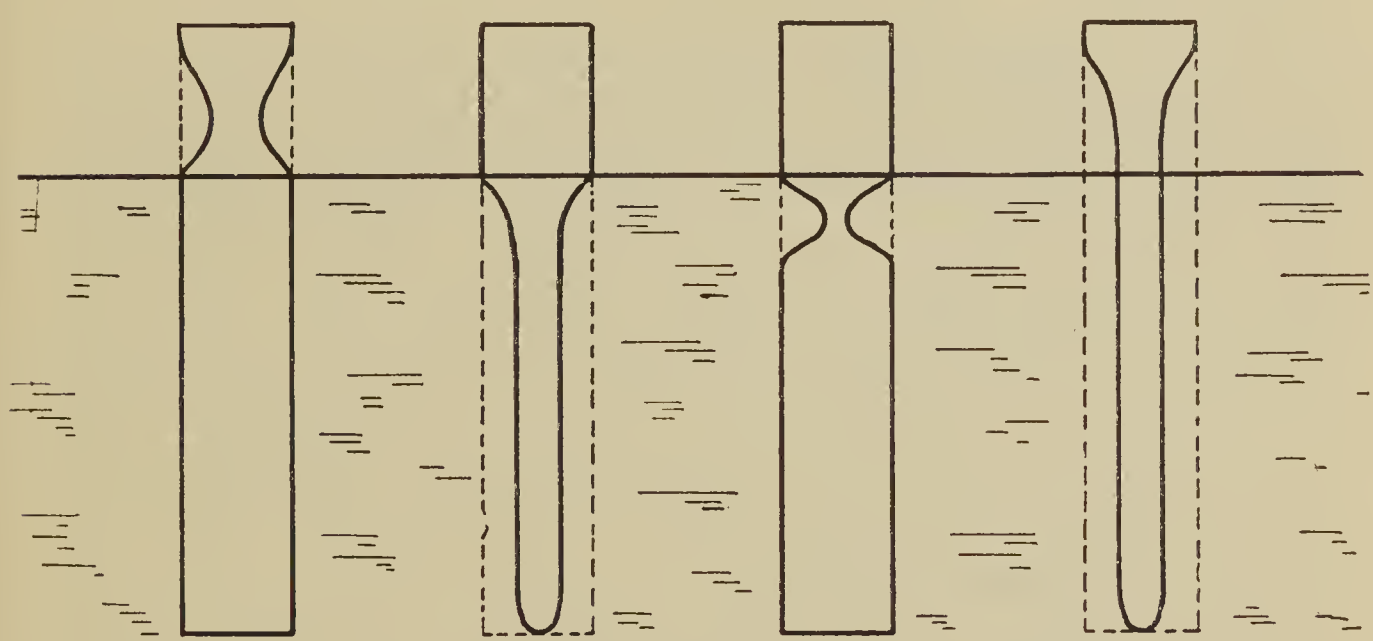

Fig. 1. Fig. 2a. Fig. 2b. Fig. 3.

Dotted lines show original contours.

to illustrate to you a very simple test which enables one to easily distinguish between ordinary chemical corrosion and electrolytic corrosion. There are three different types of alloys corresponding to three distinct types of corrosion. In the first type, upon immersing the alloy as anode into a weakly acid solution, and

[1] Consulting Electrometallurgist, So. Yonkers, N. Y.

applying a direct current of about 20 amperes per square foot of anode, the purely chemical corrosion takes place almost exclusively above the solution line. At the end of the test the anode will appear as indicated in Fig. 1. To this type belong such alloys and metals as develop a protective film during the early stages of electrolysis.

The second case is that of pure electrolytic corrosion (see Figs. 2*a* and 2*b*). The corrosion takes place below the surface of the solution and there is no corrosion above the solution line. Many of the so-called corrosion proof alloys belong to this type. If the electrical resistance of the alloy is greater than that of the solution, the anode at completion of test will take on the appearance indicated in Fig. 2*b*.

The third type is illustrated in Fig. 3. It is a combination of Types 1 and 2. Corrosion takes place above as well as below the solution line.

WM. C. MOORE[2]: There is one statement here that I can not quite agree to, and that is on page 123, the first page of this paper. He says, "When materials are exposed in the atmosphere the test conditions are as a rule highly oxidizing. The following tests were conducted under reducing conditions." Just then Mr. Aupperle proceeds to saturate his liquid with air. Now he carries in considerable oxygen when he does that, so he has all that oxygen in there to act as a corroding agent; and I do not see how he can say that these tests were under what you might call strictly reducing conditions.

J. A. AUPPERLE: The amount of sulphuric acid present in this test is sufficient to always have a preponderance of hydrogen gas, which is reducing, and in no instance did we observe any oxidizing condition as would be indicated by the brown color of the ferric salt.

J. W. RICHARDS[3]: We should bear very closely in mind that Mr. Aupperle has introduced a considerable variety of electrochemical systems into these tests. We can investigate metals for corrosion by dipping them in acid or leaving them out in the air by

[2] Research Chemist. U. S. Industrial Alcohol Co., Baltimore, Md.

[3] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.

themselves, but when we link them up with other metals electrochemically we introduce a great many different factors. There is no simple comparison possible between these results and the results of previous investigators working with the metals unconnected with other metals.

D. A. RUSSELL[4]: Just in connection with Dr. Richards' remark, I might say, in our laboratory we conducted a number of experiments in connection with problems that came up in corrosion, and we first started with those experiments by carrying them on in the same solution, that is, different metals in the same solution, in the same container; and we afterwards followed these up by isolating each metal being studied in different compartments under the same conditions of temperature, and we got very materially different results, showing that there were compounds formed that influenced the corrosion very materially.

J. A. AUPPERLE: I may add that the introduction of ferrous sulphate has changed the conditions very materially from what you get in a straight sulphuric acid, and that is one of the things we tried to show in the paper.

E. A. RICHARDSON[5] (*Communicated*): The title of this paper is much too broad and should perhaps be modified to include only the corrosion of iron and steel in mixtures of sulfuric acid and iron sulfates.

Some of Mr. Aupperle's conclusions are hardly justified by his own data. Conclusion No. 1 states that the presence of copper in iron or steel is detrimental under the conditions of his test. Tables I and II prove quite the contrary. For instance, (Table I) pure iron shows a loss of 118 grams per square meter against 134 for the same iron containing copper. Anyone who has worked with corrosion problems will, I think, admit that the slight difference between these two figures is well within the experimental errors found in corrosion work. Hence, the authors' conclusion that copper is detrimental to pure iron under the condition of their test is hardly justified.

In the case of plain and copper-bearing steel, Table I shows

[4] Chief Chemist, Youngstown Sheet and Tube Co., Youngstown, Ohio.
[5] Chemist, National Lamp Works of General Electric Co., Cleveland, Ohio.

that the presence of copper in open-hearth steel increases the rate of corrosion by about 50 percent. Table II, however, shows that copper added to an open-hearth steel is not detrimental, the figure being 243 for plain and 233 for copper-bearing steel, and that the presence of copper in Bessemer steel decreases the amount of corrosion by at least 60 percent (the loss for the specimens marked "failed" not being given they are assumed as 1016). Hence Aupperle and Strickland's conclusion that copper is detrimental to steel is also not justified.

It may be argued that in Table II the plain and copper steels are not from the same melt, yet Conclusion 3 infers that copper is the dominating factor. Either Conclusion 2 or 3 is in error.

Conclusion 4, that the authors' tests are of importance in structural work, since copper fittings are used in hot water tanks, etc., is not correct. Hot water tanks and radiators are not containers for mixtures of sulfuric acid and ferrous and ferric sulfates.

It is rather difficult to understand how these tests simulate service conditions such as tanks, boilers, boats, tubes, cables and smokestacks. Excepting under very special conditions, acid solutions similar to those used by the authors of this paper would not come into contact with boilers, boats, etc. If this paper and that by Cushman and Coggeshall prove anything, they prove that each corrosion problem is a distinct problem by itself, and results obtained under one set of conditions cannot be used to predict results under another set of conditions.

O. W. Storey[6] (*Communicated*): The results obtained by authors of this paper are very interesting in showing what may be obtained by subjecting iron and steel to special conditions, and again emphasizing the fact that the results obtained under one set of conditions usually cannot be applied to another. The error of applying data obtained under one set of conditions to other conditions has been pointed out so often that it is indeed surprising that the authors should draw conclusions so sweeping as a result of their tests. Under the summary in paragraph 6, there does not seem to be any justification for the conclusions reached. The conditions under which the iron and steel would

[6] Metallurgical Engineer, Madison, Wis.

be used in the situations enumerated in paragraph No. 6 are in many cases entirely different from the conditions under which the tests were carried out. The conclusions drawn with reference to coal and ore cars are not justified by results obtained by the Bessemer railroad in the cars which were made up partly of copper steel and ordinary steel. My own work in determining the corrosion of steels in stoves, as presented in a paper before this meeting of the Society, shows the fallacy of the conclusions with reference to the construction of smokestacks. My work has shown that the higher the copper content of the steel the more resistant does the steel become to the products of combustion under the conditions obtained in ranges. Later data show that when the conditions become such that the corrosion is much more excessive as in the case of smoke-jacks on roundhouses, it has been found that varying the copper content in the steel does not change the resistance of the steel to the products of combustion. Under these highly corrosive conditions pure iron, copper-free, low and high copper steels corroded alike, showing that there is a limiting condition above which copper is of no benefit. The results of this work were available too late to report at this meeting, but they go to show that under the excessive corrosion obtained in smoke-jacks all of the ordinary steels corrode rapidly and at about the same rate, which does not justify the use of steel in such construction. In view of the above data, immersion tests such as were carried out by the authors of this paper cannot be applied to the other conditions enumerated in paragraph No. 6. Even in the case of steel exposed to mine waters these results do not apply, since mine waters usually contain free acid and iron sulphates in quantities many times smaller than the solutions used for this investigation and which would probably give entirely different results in similar tests. Data which I collected in the Pittsburgh district six years ago indicated that even with the highly corrosive mine waters in the Connellsville district, copper steel pipe had several times the life of the ordinary steel.

Another point to be noted is that the losses in all cases were excessive and it is doubtful that steel would be used under conditions in which the corrosion is as excessive as those used by

the authors for testing purposes. In the corrosion tests previously noted in the literature in which dilute sulphuric acid was used as the corroding medium, the addition of copper greatly reduced the corrosion of steel. This does not appear to be the case with the corroding medium selected by the authors, and shows that a slight difference in the conditions of the corrosion may cause a tremendous difference in the results obtained under the new conditions.

J. A. Aupperle and D. M. Strickland (*Communicated*): We have noted with interest the communicated comments as submitted by Messrs. Richardson and Storey.

Referring to Table I where we report corrosion losses for the pure iron and the copper iron to be respectively 118 and 134 grams per square meter, a careful student will note that the copper iron has lost over 13 percent more than the pure iron. Since our results are averages and not single instances, and since our tests were carefully and scientifically conducted, this corrosion difference is far greater than an experimental error. Further, this figure is amply verified by the results reported in Table II, where the pure iron again lost but little when compared to the copper iron which failed completely. Mr. Richardson ignores the fact that Table I shows that the copper steel lost approximately 220 percent more than the pure iron.

Mr. Richardson also ignores the fact that Table II shows the pure iron to have lost the least of any of the competing grades. He seeks to divert attention from this outstanding feature by citing a resumé of the poorer resistant metals, endeavoring to show that copper additions bettered the iron or steel, forgetting that in the same table it is shown that the copper iron failed completely and that the low copper open-hearth steel is better than the copper Bessemer.

Our conclusion 3 to which he takes exception is founded on the results obtained, not in Table II as Mr. Richardson mistakenly assumes, but from results listed in the ignored Table V, which gives analyses and results in detail. He makes no mention of the conclusive results recorded in Tables III and IV.

Mr. Storey as well as Mr. Richardson take exception to our

conclusion 6, which deals with the application of our new testing methods. Both writers have read claims into this summary which are not made. They then endeavor to disprove their own mistaken assumptions—Mr. Storey, by a dissertation on smoke-stacks, which is somewhat foreign to the nature of our paper, and Mr. Richardson, by singling out a few specific figures and losing sight of the subject matter as a whole.

As clearly stated in the first four words of summary 6, this paragraph refers to our new testing methods, namely: (1) The use of a single immersion tank with equipment for circulation and aeration of the corroding liquid, thereby simulating the conditions of the mine water test conducted by the American Society for Testing Materials, and other service conditions as mentioned. (2) Riveting together specimens of dissimilar metals which yielded instructive corrosion losses when immersed in the corroding medium. Messrs. Richardson and Storey absolutely ignore the results obtained by this novel method of testing.

A study of the United States Governmental researches and analyses of acidulated river waters will show that our corroding solution was well chosen, and, although tanks may not have been originally made to hold acidulated ferrous-ferric sulphate solutions as stated by Mr. Richardson, nevertheless, repeated use of such waters with the attending evaporation, concentrations will expose the tanks and boilers to requirements which closely approximate our solution conditions. Mr. Storey mistakenly infers that different results would have been obtained had our solution been of weaker character. He ignores completely the fact that our results were wholly substantiated by the results of the American Society for Testing Materials' mine water investigation, where an analysis of the water revealed the fact that the existing percentages of acid and sulphates were hardly one-tenth as great as found in our solution strengths.

It is significant that neither Mr. Storey nor Mr. Richardson comment unfavorably on our conclusion 7, which is derived from the data obtained when the dissimilar samples were immersed in contact with each other. The data obtained showed that under such conditions the metal containing the most copper suffered the greatest corrosion losses. Since our researches prove

that copper-bearing sheets vary greatly in their copper contents, we believe that such installations of sheets (which must necessarily be in contact) will have the longest service life when this copper variable is absent and all the sheets have not only the copper but all other contaminating impurities reduced to a minimum.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

PRACTICAL MEANS OF PREVENTING CORROSION OF IRON AND STEEL WHERE NOT EXPOSED DIRECTLY TO THE ATMOSPHERE.[1]

By F. N. Speller.[2]

The Electrolytic Theory of Corrosion as formulated in 1903 by Dr. Whitney has led to the development of certain protective systems which are based on the removal of dissolved oxygen from water. Careful experiments in the Research Laboratories of the Massachusetts Institute of Technology and the National Tube Company have demonstrated that the amount of corrosion found is almost directly proportional to the amount of oxygen in solution and varies directly as the temperature. The predominating influence of free oxygen in water was suspected before this as a result of the early study of pipe corrosion, for the most striking fact in practical pipe experience is that hot water heating systems invariably show no corrosion to speak of after 35 or 40 years use whereas frequently hot water supply systems operating at the same average temperature with the same water last only 6 or 8 years. That this was independent of whether the material was iron or steel was fully demonstrated by many service tests which were conducted for a period of over ten years, in which representative pipes of each class were installed alternately in hot water lines. A few of the more recent tests by independent observers are given in Table I for reference. It is believed to be unnecessary in view of this evidence to refer in detail to older investigations recorded elsewhere several years ago.[3] Suffice it to say that all the reliable data on this subject which we have seen up to the present indicate that the composition of the iron, *i. e.*, the varying amount of carbon, phosphorus, manganese, sulphur,

[1] Manuscript received January 26, 1921.

[2] Metallurgical Engineer, National Tube Co., Pittsburgh, Pa.

[3] Comparative service obtained with wrought iron and soft steel pipes as water lines in the United States. International Association for Testing Materials, New York, 1912.

silicon, oxides, slag, and copper usually found in wrought iron and soft steel, makes very little difference on the amount or character of corrosion under water. This refers particularly to the depth of corrosion commonly known as pitting.

The location and depth of pitting seem to be mainly determined by variations of potential on the surface of the metal, principally due to the mill scale in irregular patches usually found on the surface of rolled iron or steel. Welded pipe and tubes having a particularly heavy and tightly adhering scale are on this account susceptible to pitting. It has been found by experimenting that the useful life of the tube as measured by the time to perforate is materially increased by removal of all mill scale and rust.

Several years ago, after considerable study of the influence of mill scale on corrosion of iron in service, the National Tube Company gave me the opportunity to make an attempt to remove this scale from pipe. A butt-weld pipe mill was provided with special machinery for this purpose. The pipe was made about 10 percent larger than standard, after welding it was cooled to about 1700° F. (927° C.) and passed at this temperature through a train of circular reducing rolls by which the section was reduced to standard size and the pipe elongated, thus breaking loose all scale. The usual straightening operations followed during which a light loosely adhering scale formed which has little influence on corrosion and is easily removed if desired by pickling.

In the absence of oxygen such electro-negtive materials as mill scale, oxides of iron, copper or brass have much less influence in accelerating corrosion. It is necessary to establish these points before entering on a practical consideration of the subject of protection of steel, which in the case of closed systems can evidently be accomplished in most cases by elimination of dissolved oxygen from the water.

In practice oxygen removal has been accomplished economically in two ways.

1. By de-aerating the water mechanically. This involves passing the water over baffles or spraying into a high vacuum chamber at normal temperature or by increasing the temperature and controlling the pressure and temperature so that more or less complete removal of all the gases is obtained. One system which has been proposed involves heating the water above the boiling point

corresponding to the pressure and spraying into a chamber at lower pressure. The air and aqueous vapor are drawn through a condenser where the vapor is condensed with a simultaneous transfer of heat to the incoming cold water. Almost perfect removal of gases is said to be accomplished in this way and there is no reason why nearly perfect removal cannot be thus obtained with a properly designed plant, but the condenser and other apparatus required makes such a plant quite costly and subject to severe deterioration.

For practical protection of water pipe from internal corrosion at 180° F. (80° C.) it is not necessary to have the oxygen lower than 0.4 c.c. per liter (cold water carries from 5 to 10 c.c. per liter, depending on the season of the year and temperature). For the protection of steam boilers, superheaters and economizers operating at a much higher temperature, the oxygen should be below 0.2 c.c. per liter or an appreciable amount of corrosion will occur. This may be accomplished by means of de-aerators now on the market, which are simple in construction and operate without heating the water to the boiling point. (Fig. 1.) The design of the apparatus used should be adapted to the particular conditions in each case. Several types of these are in use doing good work in the protection of iron and steel hot-water piping systems and boilers. A large system has recently been installed to de-aerate 5,000,000 gallons (20,000 cu. meters) of cold water per day for the protection of the 30-inch (75 cm.) steel main from the Darling ranges to Coolgardie Mining District, Western Australia, which is reported to have reduced the corrosion to 20 percent of that previously experienced, this being a very corrosive water.

2. The other means of protection referred to is based on fixing the free oxygen by chemical combination. This has been carried out in practice in the case of hot water systems by passing the heated water through a storage tank carrying a mass of expanded sheet iron giving about 60 to 70 sq. ft. (sq. m.) of surface per cu. ft. (cu. m.) of space. In half an hour or so at 170° F. (77° C.) the oxygen may be reduced in this way to 0.3 c.c. per liter. If the water carries free CO_2 and bicarbonates, as is usually the case, the free CO_2 contents are usually a little higher after this treatment, notwithstanding which practically no corrosion is found. My first experiments with the use of scrap iron in 1907

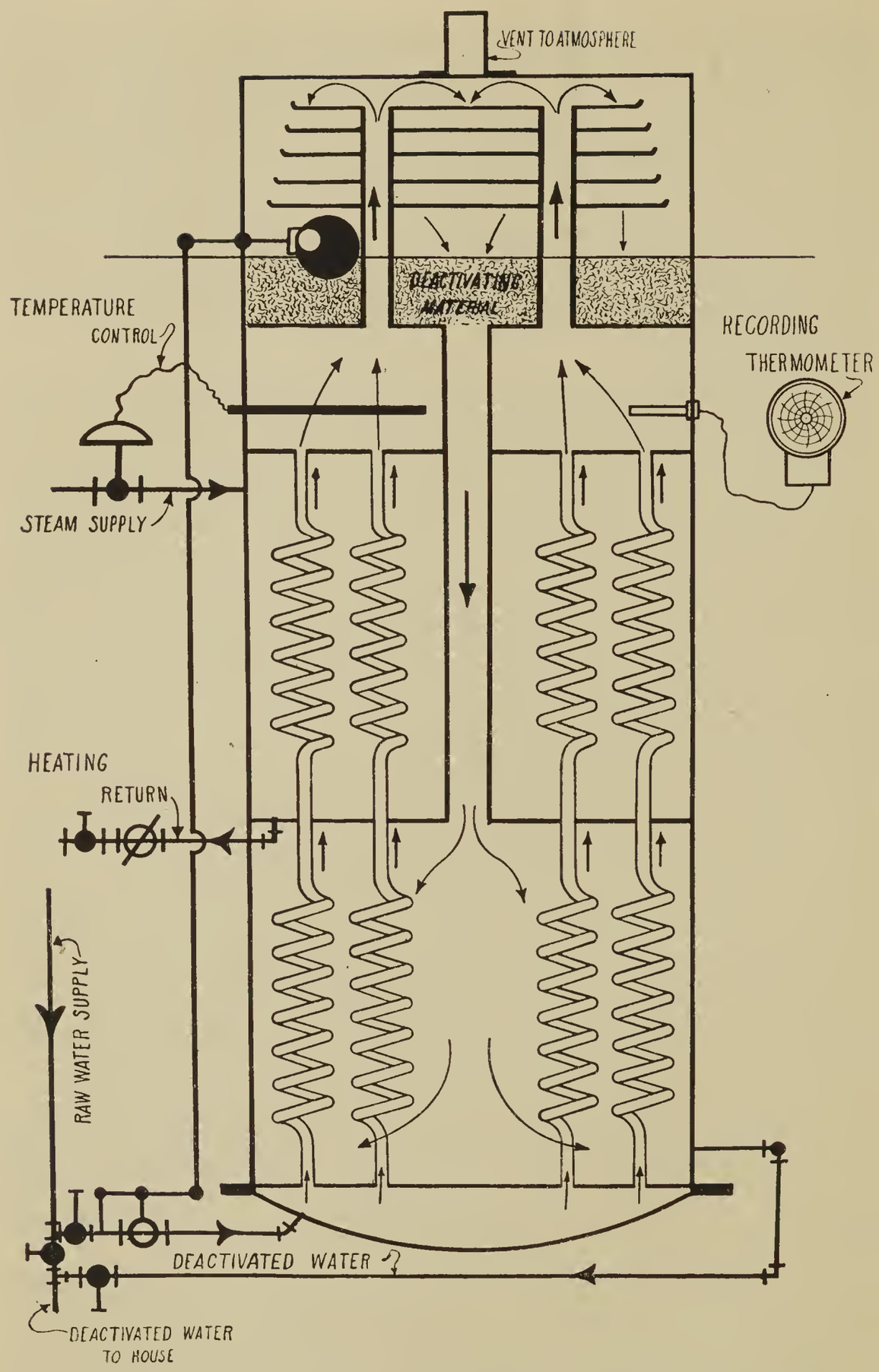

Fig. 1. In operation the cold water enters the aerator at the bottom and flows upwards through the coils, taking up some heat from the down-flowing water. The temperature of the water is raised to about 205° F. (96° C.) as it passes through the middle steam-heated compartment. From this the water rises and flows over baffles where the air is nearly all separated, the residual oxygen being removed by some suitable de-activating material before the water passes downwards to the outlet, the temperature being reduced to about 150° F. (66° C.) in passing through the lower heat exchanger.

were made with steel turnings, which after a time clogged up tightly into an impermeable mass. This difficulty was overcome by the use of expanded steel sheets suitably formed so that they would not pack tight. The first plant of considerable size based on this principle was designed and built by the author in Pittsburgh in 1915, and has now been in successful operation for over five years; the essential features of this apparatus are indicated in Fig. 2. For domestic use the water after this treatment should be filtered.

This method of "de-activation" (the term by which I have suggested to designate this process) may be used to supplement mechanical de-aeration as described above, which combination seems to be the most ecnomical means for oxygen removal from hot water on a large scale under average conditions. For example, take a power plant equipped with open-feed water heaters operating at 180° F. (80° C.); it will be found possible by means of the heaters alone to reduce the free oxygen in the feed water from 8 c.c. to 2 c.c. per liter. If the water space of the heater is filled with thin steel lathing or the water be made to flow through another tank containing steel scrap in this form, the residual oxygen will be fixed in a few minutes. Water so treated is practically inactive towards iron, and may be used in boilers or steel economizers without fear of corrosion so far as the water is concerned. Other metals may be used for oxygen removal, such as zinc, but iron is the most economical, not only because of its low first cost but for the reason that the ferrous hydrate formed removes an equivalent of oxygen in addition to oxygen taken up by the hydrogen. Furthermore it has been proved to be true, as would be inferred from the above, that the corrosion of zinc, brass and other metals is greatly retarded if not entirely stopped by the removal of oxygen from the water which comes into contact with these metals.

Brass and copper piping are seriously attacked by heated water under pressure. For example, we find that the water which is heated for our laboratory in a copper coil heater of the usual type loses nearly one-half of its free oxygen in passing through this heater and brass pipes which after ten or twelve years are frequently found to have lost nearly all their zinc contents. The

same has been observed with alloy-condenser tubes, so that there is apparently an important field for the application of these principles of protection to brass and copper piping systems.

In connection with our tests in Pittsburgh we placed some zinc,

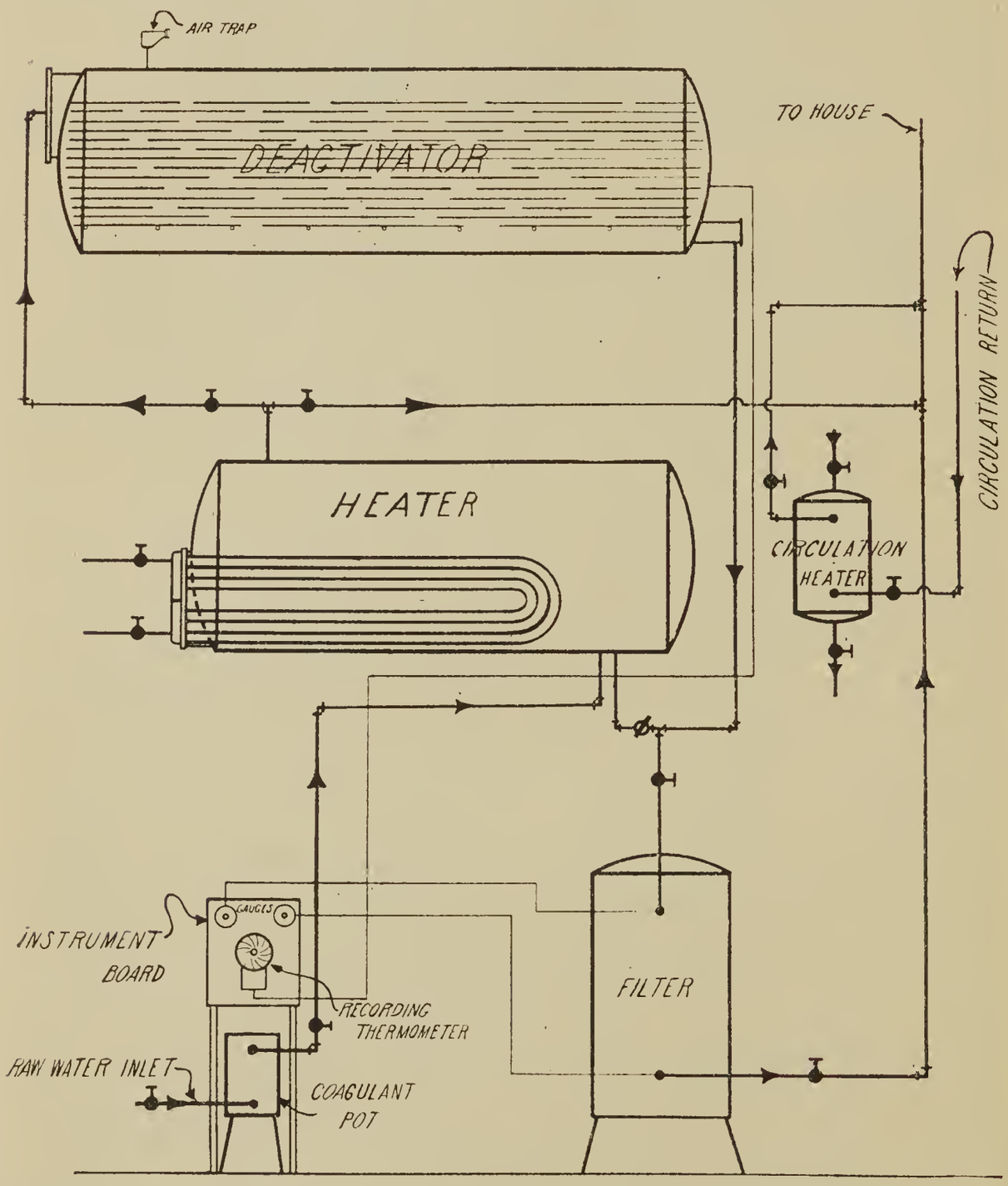

FIG. 2. In this system the oxygen is removed by combination with scrap steel sheets in the upper tank (the de-activator). The heater circulating pipes and filter are shown.

brass, and steel-brass and steel-copper plates in contact in raw and de-activated hot water service for one year with the losses in weight shown in Table I.

The accelerating effect of copper and brass in contact with steel

under these conditions has been greatly reduced by the lack of a depolarizer, as would be expected, and it will be noted that the loss in weight of the steel when in riveted contact with copper

TABLE I.

Weighed Test Pieces in Hot Water Lines.

Comparative corrosive action of deactivated and of untreated water at Irene Kaufmann Settlement, Pittsburgh, Pa., on (1) zinc plates, (2) brass plates, (3) steel and brass plates coupled together, and (4) steel and copper plates coupled together. Test finished January 14, 1919.

Test	Piece No.	Original Weight Grams	Final Weight Grams	Loss in Weight Grams	Loss Grams per sq.in.
(1) Zinc plates 2x6x¼ in...	DD-4	348.15	314.70	33.45	1.194*
Area—28 sq. in.	DD-5	351.62	320.90	30.72	1.097*
Time—12 months, 52 days..	DD-6	350.82	316.35	34.47	1.231*
Avg. temp. about 160° F....	DD-1	Lost			
	DD-2	352.20	348.10	4.10	0.146†
	DD-3	351.00	346.50	4.50	0.161†
(2) Brass plates 2x6x$\frac{1}{16}$ in..	BB-1	108.87	108.50	0.37	0.011*
Area—25 sq. in.....	BB-2	105.50	103.65	1.85	0.074*
Time—12 months, 52 days..	BB-3	107.00	105.95	1.05	0.042*
Avg. temp. about 160° F....	BB-4	107.08	107.00	0.08	0.0032†
	BB-5	103.97	103.90	0.07	0.0028†
	BB-6	108.15	108.09	0.06	0.0024†
(3) Steel and Brass plates (1¾x4x$\frac{1}{32}$ in.) coupled together with brass rivets at one edge. Area—14 sq. in.	Brass-C-3	28.893	28.391	0.502	0.036*
	Steel-C-3[1]	16.008	0.00	16.008	total loss*
Time—12 months, 10 days.	Brass-C-4	29.474	29.463	0.011	0.0008†
Avg. temp. about 160° F....	Steel-C-4	15.809	13.268	2.541	0.1815†
(4) Steel and Copper plates (1¾x4x$\frac{1}{32}$ in.) coupled together with copper rivets at one edge. Area 14 sq.in.	Copper-B-3	16.535	16.368	0.167	0.0119*
	Steel-B-3[1]	16.128	0.00	16.128	total loss*
	Copper-B-4	16.444	16.416	0.028	0.002†
Time—12 months, 10 days.	Steel-B-4	16.623	13.255	3.368	0.2405†
Avg. temp. about 160° F....					

[1] Steel pieces C-3 and B-3 were entirely corroded away.

* In untreated water line. † In de-activated water line.

and brass is very little more than that suffered by the insulated zinc plates in de-activated water under the same conditions. In this experiment the test pieces were placed in two horizontal steel

TABLE II.

Summary of Results of Investigations of the Corrosion

Date	Locality	Length of Time Pipe Lines Were Installed	Authority and References
1919	Irene Kaufmann Settlement, Pittsburgh, Pa.	2 yrs., 7 da.	Jas. O. Handy, Technical Director, Pi burgh Testing Laboratory. Report ma to Resident Director Teller, Jan. 1920; p. 97, Jan., 1920, A. S. H. & Engrs.; p. 276, Mar., 1920, A. S. H. V. Engrs.
1919	Harvard University, Cambridge, Mass.	3 yrs.	Melville C. Whipple Inst. in San. Che Harvard University. Jrn'l New Engla Water Wks. Asso., p. 42, Mar., 1920.
1919	Irene Kaufmann Settlement (2d Test), Pittsburgh, Pa.	1 yr., 2 mos.	Jas. O. Handy, Technical Director, Pi burgh Testing Laboratory. Report Pittsburgh Testing Laboratory, April 1918, p. 217, 1918 Trans. A. S. H. & Engrs.
1918	Brown University, Providence, R. I.	11 mos.	Wm. F. Kenerson, Professor of Mecha cal Engineering, Brown University. port made June 7, 1918. Bulletin 2 "Corrosion of Hot Water Piping." N tional Tube Co.
1917	This test was conducted in four different places as follows: (A) West 41st St. Bath, New York. (B) East 76th St. Bath, New York. (C) East 109th St. Bath, New York. (D) Cherry and Oliver Sts. Bath, New York.	 2 yrs., 9½ mos. 2 yrs., 5 mos. 2 yrs., 6 mos. 2 yrs., 6 mos.	James S. Macgregor, Instructor in Ci Engineering, Columbia University. port made Jan.-March, 1917. Bulletin —"Corrosion of Hot Water Piping National Tube Co.
1916	Irene Kaufmann Settlement, Pittsburgh, Pa.	11 mos.	Jas. O. Handy, Technical Director, Pi burgh Testing Laboratory. Report ma December 6, 1916. P. 125, 1917 Tra of A. S. H. & V. Engrs.
1916	Irene Kaufmann Settlement, Pittsburgh, Pa.	10 mos.	Jas. O. Handy, Technical Director, Pi burgh Testing Laboratory. Report ma October 31, 1916. P. 125, 1917 Tra of A. S. H. & V. Engrs.

A grand average of the entire seven tests tabulated above shows the avera steel pipe, 0.0632 in., or a difference of 0.01

Table II.

ught Iron and Steel Pipe in Hot Water Supply Service.

umber of Cases on Record	Average of Deepest Pits Inches		Conclusions
	Wrought Iron	Steel	
u lengths of steel, 15 s of wrought iron ar- l alternately.	0.1144	0.1095	"These figures show that no marked distinction is possible between the rate of corrosion of the steel and the iron pipe."
ections each of scale- teel); galvanized steel, steel and wrought ipe.	0.073	Scale Free 0.045 Copper 0.068 Galvanized 0.078	"Judging from the depths of pitting and the general appearance of the inside of the pipe, it was evident that, so far as the conditions of this particular experiment with the Cambridge hot water service were concerned, scale-free pipe had suffered less real damage than any of the others after three years' exposure."
ctions each of steel rought iron pipe.	0.122		"This test and other similar tests have shown beyond question that in the Pittsburgh district wrought iron and steel pipes in hot water lines are rapidly corroded by pitting and that the laminated or fibrous structure of wrought iron produced by the included layers of slag, does not give any added durability to wrought iron, as compared with steel pipe."
ections each of "Na- " black and copper nd wrought iron; one each of "National" zed and copper alloy, zed.	0.0674	"National" (Black) 0.0544 Copper Alloy 0.0639 Galvanized 0.0547 Copper Alloy Gal. 0.0938	"There is evidently no marked superiority of either the wrought iron or steel for the test conditions described. . . . The wrought iron failed first by developing the deepest pits. The steel developed a greater number of shallower ones."
sections each of t iron and steel pipe. sections of steel and wrought iron pipe. me as test B. ne section each of nd copper steel.	(A)0.057 (B) 0.075 (C) 0.061	0.052 0.070 0.035 (D) Steel 0.021 Copper Steel 0.022	Taking the total averages of steel (which includes scale-free and copper steel as well as ordinary black) pipe as against those for iron in the four tests we find the latter to have pitted deeper by 0.025 in., which indicates in favor of steel pipe in these particular tests.
ctions of steel, one of zed steel and one of t iron pipe protected xidizent; 2 sections steel and wrought pe not so protected.	Protect 0.045 Unprote 0.082	ed by Deoxidizer (Galvanized) 0.040 (Black) 0.028 cted by Deoxidizer 0.070	This test had as its chief aim a study of the protection of pipe by use of a deoxidizer, and the author does not draw direct conclusions on the comparative corrosion of the iron and the steel pipe. The figures on depth of pitting, however, stand in favor of steel pipe.
sections of steel and rought iron pipe.	0.121		The author states that a certain sample of wrought iron showed the most general corrosion, while a steel section showed the greatest number of separate pits. No direct reference to comparative corrosion is made.

est pits to have been, for the wrought iron, 0.0817 in., and for the 23 percent in favor of the steel pipe

water lines, one carrying raw water with about 6 c.c. per liter of oxygen and the other water with an average free oxygen content of about 0.3 c.c. per liter.

The rate of corrosion may be retarded by increasing the proportion of hydroxyl ions with relation to the hydrogen ions present in the water. In practice in the case of boiler water this can be carried out by the use of 5 to 10 gr. per U. S. gallon (86 to 172 mg. per liter) of caustic lime or soda ash, but with domestic water it is possible to use only a comparatively small amount of alkali and the protection afforded is proportionately lessened. Great Lakes water with about 8 gr., per U. S. gallon (137.6 mg. per liter) of calcium carbonate is very much corrosive than New York City water with 1 or 2 gr. per U. S. gallon (17.2-34.4 mg. per liter) of carbonates, although each have about the same amount of oxygen. There are cases where natural waters used for cooling purposes in condensers or transformers may have their corrosive activity reduced with economy 50 percent or more by passing the water through a bed of crushed limestone, but this treatment is not nearly so effective as partial de-aeration and may cause an insulating scale to form if this treatment is carried too far.

The more important research on the subject of relative corrosion of piping in hot water feed service that has been accomplished within the last five years is summarized very briefly in Table II.

DISCUSSION.

T. S. Fuller[1]: I would like to ask Mr. Speller if he has found that he can deactivate cold water for use in hot water systems?

F. N. Speller: Yes, you can do that by using a vacuum chamber, and using a fairly high vacuum. This has been done successfully in Australia in connection with a pipe line which suffered very seriously from corrosion. The temperature of the water was about 18° C., and they rigged up, at a suitable level, a vacuum chamber, using about 28 inches of vacuum, and got

[1] Metallurgist Research Lab., General Electric Co., Schenectady, N. Y.

90 percent of the oxygen out before passing the water through the pipe line. The result has been that they have cut down corrosion about 80 percent.

T. S. FULLER: If for any reason you should want to use this deactivated water in a cold system, you would pass it cold over scrap iron, would you?

F. N. SPELLER: It depends on what kind of a system it is. Remember, that in passing water over iron you discolor the water by the formation of colloidal iron. We must usually filter deactivated water if it is going to be used for domestic purposes, but it is all right for boiler purposes in its natural condition unfiltered.

A. S. CUSHMAN[2]: There is only one point where I would want to express a difference of opinion with Mr. Speller. I am not willing to concede that a homogeneous, non-segregated, well-made ferrous metal will not be superior in corrosion resistance to one in which those particular points are not paid attention to. I do not think that Mr. Speller would claim, for instance, that a non-crop ingot could be rolled into as successful a pipe as steel in which the metallurgist has paid attention, from the beginning of the heat to the end of the pour, to the points of achieving as high a degree as possible of de-gasification, homogeneity, and freedom from segregation. I do not think, practically speaking, that it is right to give the impression that those points are not important when we are considering manufacturing material for slow-rusting or corrosion-resistance purposes.

F. N. SPELLER: In regard to Dr. Cushman's point of controversy on the effect of homogeneous metal, I rather think he overdraws the importance of this factor. However, I am not entirely out of accord with him on this point. Everything else being equal, there is no doubt that a homogeneous metal is more desirable than one that is heterogeneous, and we all strive, of course, to the highest possible degree of uniformity, but when you consider the factors which cause pitting in a piping system, for example, or in boiler tubes, the effect of segregation is almost negligible, within the ordinary commercial limits that will allow

[2] The Institute of Industrial Research, Washington, D. C.

the tube or pipe to pass the standard specifications, compared with the effect of surface condition due to mill scale, rust, mechanical distortion and other irregularities. I say almost negligible, but when you consider the effect of removing, say 50 to 90 percent of the oxygen, the influence of segregation, if any, is still further reduced. I do not want Dr. Cushman to leave the impression that we want to excuse poor material. That is not the idea at all. On the contrary, I am as strong for a high standard of quality as anybody. We have been trying to control corrosive conditions that apparently cannot be controlled in any other way. Composition of the metal seems to have very little influence on corrosion under water.

Colin G. Fink[3]: Mr. Elliott Cumberland,[4] of England, was interested in Mr. Speller's paper and he sent us a discussion. In the Cumberland method they put the iron plate right into the boiler tube rather than placing it outside in a separate container. Mr. Cumberland is very outspoken in condemning zinc, and I see that Mr. Speller uses zinc in his process for removing the last traces of oxygen. Why use zinc? Would not iron do just as well?

F. N. Speller: Because zinc will not discolor the water as much as iron. Iron is preferable and more economical and is always recommended for power plant work or domestic water, but in the latter case a filter is usually required.

A. S. Cushman: In this deactivated water that has been filtered, is there iron in solution?

F. N. Spellers Yes, a very slight trace, not more than 0.2 part per million.

A. S. Cushman: Can you taste that iron?

F. N. Speller: Oh, no. The first effect of iron is noticed in laundries, when the water carries 0.3 part per million or more.

Elliott Cumberland (*Communicated*): In my system which has been introduced in England, insulated iron anodes are immersed within the structure to be protected. These anodes are connected to a D. C. generator and each anode is

[3] Consulting Electrometallurgist, So. Yonkers, N. Y.
[4] The Cumberland Engineering Co., London, E.C.3, England.

controlled by a separate resistance for regulating the current to a suitable density. The surface which it is desired to protect is connected to the negative pole of the generator. A film of hydrogen is formed on the immersed surface of the unit to be protected. The hydrogen not only protects the surface from corrosion, but its mechanical action between the metal and the scale carries away into solution all dirt, scale and grease adhering to it.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

THE EFFECT OF COPPER AND SILVER SALTS ON THE CORROSION OF IRON BY ACIDS.[1]

By Oliver P. Watts[2] and Harold C. Knapp.[3]

Abstract.

A record of tests on the corrosion of iron by sulphuric acid in the absence or presence of various salts of copper and silver. The conclusion drawn is that in general corrosion is stimulated by the presence of these salts. The theory of this action is discussed. A remarkable example of electrochemical corrosion in sea-water is given. [J. W. R.]

There is a time-honored belief, quite generally held by those who have studied corrosion, that the addition of a copper or a silver salt accelerates the corrosion of iron by sulphuric acid. This acceleration is supposed to take place in two ways: First, the metal of the dissolved salt is replaced by iron, thus causing direct corrosion of the latter; second, the copper or silver precipitated on the surface of the iron sets up a voltaic couple with the iron as anode and the other metal as cathode, and if the discharge potential of hydrogen on the new cathode is less than on iron, as is the case with copper and silver, corrosion is stimulated.

In a detailed paper on the solution of metals by acids presented at the 38th meeting of this Society in October last, W. D. Richardson reported the results of experiments on the corrosion of iron by normal sulphuric and hydrochloric acids, with and without the addition of salts of copper and silver. Speaking of this voltaic or "catalytic action," as he calls it, of silver salts, he says, "No noticeable effect was produced on any of the metals tried in

[1] Manuscript received February 26, 1921.

[2] Assoc. Prof. Chem Eng., University of Wisconsin.

[3] University of Wisconsin.

hydrochloric or sulphuric acids." Regarding the action of copper salts he says, "The copper was added in the form of chloride, sulphate and nitrate to the respective acids, 10 grams of metallic copper being present per 100 liters of acid. In hydrochloric and sulphuric acid none of the iron plates showed any change of rate." Further he says, "According to the older view of the electrolytic theory, copper in contact with pure iron ought to catalyze positively in non-oxidizing acids, but this is not the case. Its effect on the purer metals is negligible, nor does it affect the cast metals appreciably in non-oxidizing acids." Unfortunately the implied newer view of the electrolytic theory, according to which copper and silver salts should exert no accelerative effect on the corrosion of iron by acids does not appear in the paper, and the reader is left to wonder what this can be.

TEST I.

In $N.H_2SO_4$ with Addition of $CuSO_4$.

No.	Material	Grams Cu/Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
1.	Copper steel	0	0.0635	.....	.....
2.	" "	2.5	0.7517	0.2486	3.92
3.	" "	0.1	0.1348	0.0538	0.85
4.	Ordinary steel.....	0	5.5074	.....	.....
5.	" "	2.5	5.9947	0.0477	0.008
6.	" "	0.1	5.5886	0.0637	0 011

Having previously conducted a few experiments on the effect of copper sulphate on the corrosion of iron by sulphuric acid, the authors could not accept the above statements as representing the facts, and therefore the experiments reported below were carried out.

The materials used for corrosion were ordinary sheet iron (probably a mild steel) purchased at a local hardware store, copper steel supposed to contain about 0.25 percent of copper, and Armco iron. The test pieces, 5 cm. square, were pickled in pure sulphuric acid to remove scale, dried, weighed, and immersed in an upright position in 200 c.c. of acid at 30° C. for 24 hours. A sufficient quantity of copper sulphate or silver carbonate was in

some cases added to give either 2.5 or 0.1 grams of metal per liter. The latter amount was that used by Mr. Richardson. The loss by voltaic or catalytic action is calculated by deducting from the total loss in weight the amount of iron that should be dissolved by the metallic salt added, and also the loss caused by the acid alone in the same test.

It is seen that with the larger amount of copper voltaic action is nearly four times the direct corrosion by the acid, but with the smaller quantity of copper voltaic action is somewhat less than corrosion of the copper steel by the acid. With ordinary steel voltaic action is about the same for either amount of copper, and although this is about the same in amount as for the copper steel, it plays an utterly insignificant part in the total corrosion, because of the tremendous corrosion by the acid.

Test II.

In $N.H_2SO_4$ with Addition of Ag_2CO_3.

No.	Material	Grams Ag./Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
7.	Copper steel	0	0.1001	.....	.....
8.	" "	2.5	0.3696	0.0111	0.11
9.	" "	0.1	0.4311	0.3207	3.2
10.	" "	0.01	0.2751	0.1733	1.73
11.	Ordinary steel....	0	5.6545	.....	.....
12.	" "	0.1	5.5677	—0.1043	—0.018
13.	" "	0..01	5.5764	—0.0798	—0.014

The figures of Test II apparently indicate less action by the large amount of silver salt than by either of the lesser quantities. This anomaly is explained by the observation that specimen No. 8 was surrounded by a spongy deposit of silver an eighth of an inch thick. This served as a diaphragm and retarded the diffusion of acid to the steel. With ordinary steel the presence of a silver salt diminished corrosion—probably by lessening the surface of steel directly exposed to the acid.

With the lessened rate of corrosion due to more dilute acid, although the loss by voltaic action is but slightly changed, it is relatively more important.

Test III.

In N/50.H_2SO_4 with Addition of $CuSO_4$.

No.	Material	Grams Cu/Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
16.	Copper steel	...	0.0296	.....	....
17.	" "	2.5	0.5802	0.1110	3.75
18.	" "	0.1	0.1307	0.0936	3.16
19.	" "	0.01	0.0576	0.0263	0.89
20.	Ordinary steel....	0	0.0669	.....	....
21.	" "	2.5	0.5904	0.0839	1.25
22.	" "	0.1	0.1234	0.0390	0.58
23.	" "	0.01	0.1030	0..0344	0.51

Test IV.

In N/50.H_2SO_4 with Addition of Ag_2CO_3.

No.	Material	Grams Ag./Liter	Loss in Grams by Corrosion		Corrosion Ratio Cat./Acid
			Total	By Catalysis	
26.	Copper steel	0.	0.0429	.....	....
27.	" "	0.1	0.1119	0.0515	1.20
28.	" "	0.01	0.1025	0.0579	1.35
29.	Armco iron	0	0.0234	.....	....
30	" "	0.1	0.1072	0.0663	2.83
31.	" "	0.01	0.0622	0.0371	1.59
32.	Ordinary steel....	0	0.0828	.....	....
33.	" "	0.1	0.1180	0.0177	0.21
34.	" "	0.01	0.1130	0.0285	0.34

Test V.

In N/50.H_2SO_4 with Addition of $CuSO_4$.

No.	Material	Grams Cu/Liter	Loss in Grams by Corrosion		Ratio Cat./Acid Corrosion
			Total	By Catalysis	
35.	Copper steel	0	0.0876	.....	....
36.	" "	0	0.0903	.....	....
37.	" "	0.1	0.2932	0.1867	2.10
38.	" "	0.1	0.2732	0.1667	1.87
39.	Armco iron	0	0.0603	.....	....
40.	" "	0	0.0680	.....	....
41.	" "	0.1	0.2461	0.1645	2.57
42.	" "	0.1	0 2869	0.2053	3.20
43.	Ordinary steel....	0	1.7340	.....	....
44.	Stove-pipe iron..	0	1.7948	.....	....

Tests IV and V show voltaic action on the more resistant metals to be from 1 to 3 times the amount of corrosion by the acid. The corrosion of duplicate specimens in test V varies by 3 percent for copper steel in acid alone and by 11 percent in the presence of copper sulphate; similar variations for Armco iron are 7 and 16 percent. These wide variations indicate that great caution must be exercised in ascribing observed differences in corrosion to the presence or absence of some metal in the alloy or to the presence of some particular chemical in the electrolyte. As a

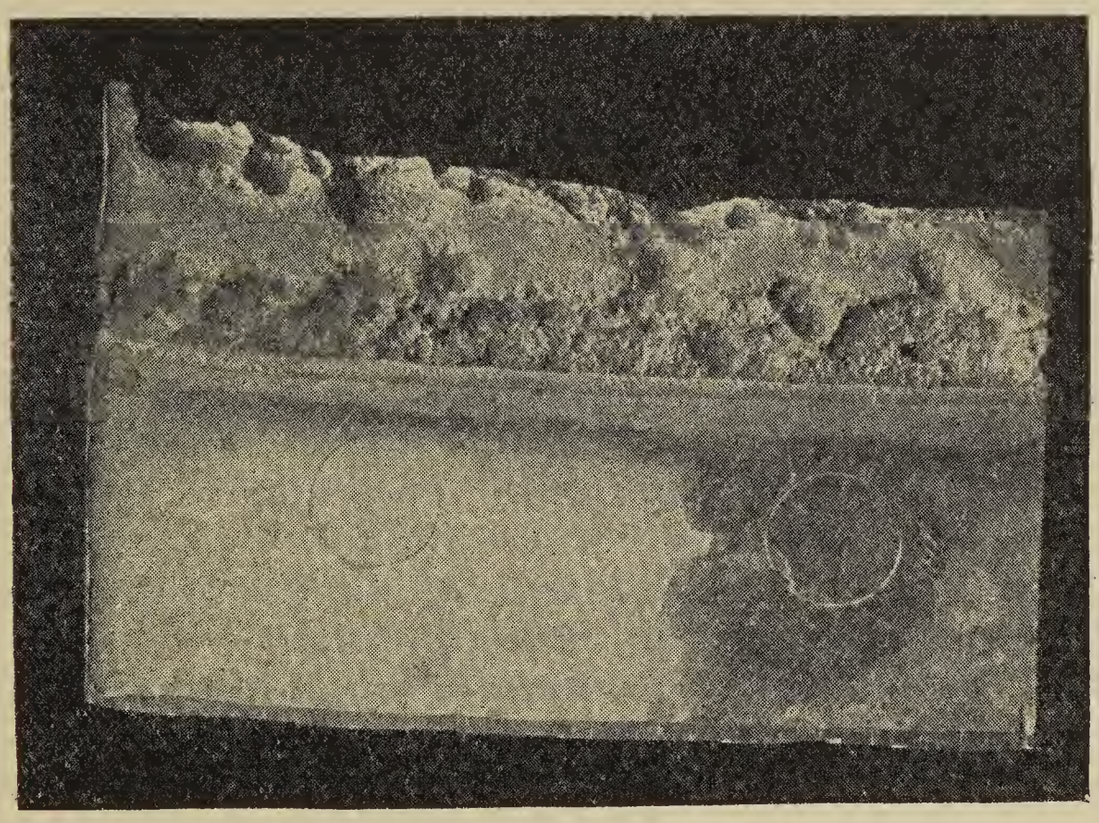

Fig. 1.

whole these experiments indicate that voltaic action by copper and silver does stimulate the corrosion of iron and mild steel by acids, particularly in the case of the more resistant materials.

Electrochemists recognize that the relative position of two metals in the electrochemical series does not entirely determine the magnitude of voltaic corrosion, but that this is affected by the extent of surface of the cathode, by the discharge potential of hydrogen on the cathode, by the presence or absence of oxygen to act as a depolarizer, by the resistivity of the electrolyte, by

the formation of protective films on the anode, etc. Yet the difference of potential between the metals is the fundamental cause of corrosion, and the other conditions are merely modifiers of its action. That ignorance of the serious effects of voltaic action and incorrect conclusions drawn from faulty experiments may have disastrous results is shown by the sad fate of the "monel metal yacht," *Sea Call.* The outside of this big schooner was made of monel, a nickel-copper alloy, with the exception of the stem, keel, sternpost and rudder frame, which were steel. Fig. 1 shows what happened. This is a photograph of the contact between a monel plate and the after side of the steel rudder frame. In three months afloat holes were eaten entirely through the steel, three-quarters of an inch thick, and it was apparent that this would soon have been entirely destroyed. Other exposed steel parts were similarly affected; the vessel was condemned as unseaworthy and was broken up without having made a single voyage. An important factor in this remarkable case of corrosion was the enormous size of the cathode (monel) in comparison with the anode (steel). The hydrogen, plated out on the monel by the dissolving of the steel, was distributed over such a great surface, and so much dissolved air was present that polarization by hydrogen must have been almost entirely prevented. As a result, the initial E. M. F. of the couple was available for producing current, which is rarely the case with accidentally-occurring couples.

This $500,000 experiment in corrosion should serve as a warning of the seriousness of long-continued voltaic action in a good electrolyte, and it should be recognized that electrochemical theory affords a better basis for predicting what will occur when a voltaic couple of two particular metals is exposed to sea water for months, than do laboratory experiments of a few hours, or even days, duration.

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University of Wisconsin.

DISCUSSION.

W. D. Richardson[1]: This paper has for consideration some work that I did and reported to this Society at its last meeting.

[1] Chief Chemist and Chem. Engr., Swift & Co., Chicago, Ill.

Certain experiments that I made showed that copper, when present to the extent of one-tenth of a gram of metal per liter of acid, did not accelerate the solution of certain samples of iron and steel in hydrochloric and sulphuric acid. The authors of this paper have reported experiments which show that in some cases copper and also silver does accelerate the action, but I should like to call attention to the point that in some of their experiments they show no accelerated action, particularly those shown on pages 156 and 157, the last two figures in the last column in each case. In one of these instances, the amount of copper used was the same as the amount I use, and in another case the amount was two and one-half times as great, and yet they report no essential change of rate to action of the copper, which is exactly what I reported.

In other instances they do find increased action. Naturally, I do not want to go on record as believing that in no case can copper accelerate corrosion, but I think we should consider the fact that copper does behave with a most peculiar manner in connection with corrosion, and this is shown by the effect of copper in copper steel, for instance. Again I conducted experiments in which I added the same amount of copper to normal nitric acid, and in this acid not only did copper not increase the rate of corrosion, but it decreased it very materially, almost one-third. It acted in a negative manner when present in a normal oxidizing acid, whereas, in my experiments, it did not change the rate in a non-oxidizing acid, and I suggested that possibly there was some connection between the behavior of copper in connection with an oxidizing acid and its behavior in copper steel under oxidizing conditions, that is, atmospheric conditions. The authors of this paper apparently take exception to the fact that it speaks of catalytic action in these cases, and they suggest, by inference, at least, that I should say voltaic action. I have no objection to that at all, except that in the paper which they are considering, I also considered the effect of formaldehyde in connection with these acids; and sometimes formaldehyde acts as a negative catalyst, and sometimes it does not change the rate. Now I wanted to call all these things by one name, and since catalytic action is the phrase which cloaks our ignorance, under these conditions I called it catalysis. The authors also apparently took exception to the statement as follows: (I am

quoting my own words) "According to the older view of the electrolytic theory, copper in contact with pure iron ought to catalyze positively in non-oxidizing acids." These authors then remark, "Unfortunately the implied newer view of the electrolytic theory, according to which copper and silver salts should exert no accelerating effect on the corrosion of iron by acids does not appear in the paper, and the reader is left to wonder what this can be."

I did not mean to imply any new view according to which copper and silver salts should exert no accelerative effect. I wish, and I have often wished, in the course of my experiments, that these things would behave according to theory, it would simplify our work. Matters do not occur according to the simple idea or the simple conception of the electrolytic theory of corrosion as advanced in the early days, and that is what I meant when I spoke of the older view of it. The recent view, and it is coming more and more into prominence, is that while this older view of a simple electrolytic theory is at the basis of all corrosion phenomena, there are so many modifying, upsetting and antagonizing influences that it does not take a straight course as we might expect if we had no further knowledge of it. Let me call your attention to one upsetting influence, rust, which I have emphasized over and over again, may accelerate, in a general way, the corrosion of iron. If it forms a closely adherent layer of the physical nature of a paint film over the entire surface, it may stop corrosion by preventing the access of water or oxygen, and if it is tightly adherent in patches, it may cause deep pitting. Now here we have the same general influence acting in different ways, in all instances upsetting the ordinary action of the corrosive substances and elements.

I believe we have another influence to contend with which may act in different and perhaps antagonistic ways, namely, oxygen. We know that oxygen is the chief disturbing influence in ordinary corrosion; it is the principal substance which causes corrosion to go in some other way than we might expect from the simple theory. We know that the corrosion of iron goes on at practically the zero rate in the absence of oxygen and in the presence of water, and we know it may go on very rapidly in the presence of pure oxygen and less rapidly in air. We know, too, that the

influence of oxygen or an oxidizing agent on the surface of iron may be such as to produce the passive condition, and when this condition supervenes, the iron behaves as monel metal and there is no corrosion at all. I have been led to suspect by some phenomenon, that I have mentioned in an earlier paper in connection with some work on cast iron, that a modified passivity may supervene in instances where we have not suspected it. I do not know that this theory explains it, but in the case of cast iron we have some very peculiar rust-resisting properties, and it may be that under certain conditions the iron coupled with graphitic carbon and under oxidizing conditions may assume, temporarily at least, or from time to time, or intermittently, a passive condition which may stop the corrosion. In discussion with Dr. Burgess last evening on the subject of copper steel, I spoke with him about the experiments which I had made, adding copper to normal nitric acid, with the result that the corrosion rate was lower, and he suggested that possibly in that case passivity was induced. I then spoke to him about the effect of graphitic carbon on cast iron, and it may be that in the case of the copper steel, we have an induced passivity, or partial passivity, or intermittent passivity, which may account for the action of the copper in that instance. I think none of us can afford to be at all dogmatic in our discussions of corrosion, and particularly when we are dealing with a metal like copper of proved peculiar behavior.

Colin G. Fink[2]: The general condition of our corrosion research today is not very inviting. Reports cannot readily be compared, as methods of investigation are so different. The investigator usually has to start out to prove a definite thing, and he must carry out his experiments along a certain line. He must prove that his company's product is good. Now if the tests do not fit into this formula, they are either not carried out or not published.

W. D. Richardson: I want to say a word in regard to the differences between hydrochloric acid and sulphuric acid. We regard them both as non-oxidizing acids. If any one will refer to my paper, "The Gap Between Theory and Practice in the

[2] Consulting Electrometallurgist, So. Yonkers, N. Y.

Production of Corrosion-Resisting Iron and Steel," and later papers, he will find that in some experiments I made I used sulphuric acid in connection with aluminum plates; with Duriron plates, it was shown that sulphuric acid behaves very similar to nitric acid. In other words, sulphuric acid seems to be able to act as though there were no oxygen influences present. We cannot set up passivity in the presence of an alkali; we can set it up in the presence of an acid.

J. A. AUPPERLE[3]: I would like to call attention to the fact that very often conclusions are drawn from insufficient data, and in this paper "the materials used for corrosion tests were ordinary sheet iron, probably a mild steel, purchased at a local hardware store, copper steel supposed to contain about 0.25 percent of copper and Armco iron." No analyses are given; therefore I do not believe the conclusions are justified from the information at hand.

Our researches seem to check Mr. Richardson's that the contact of copper has considerable influence on the rate of corrosion, retarding it in one instance and increasing it in another. The photograph on page 159 is very interesting. The authors have called attention to the great difference in the size of the electrode, the electro negative metal, steel, being extremely small, while the electro positive monel metal was extremely large. This is a very important point and undoubtedly has considerable influence on the rate of corrosion.

G. W. COGGESHALL[4] (*Communicated*): The authors show by their tabulated results that what they called voltaic action by copper and silver salts does stimulate the corrosion of iron and mild steel by acids. Their tables also show more definitely, however, another point. In the $N/50$ solution of H_2SO_4, as shown in tests IV and V, the plain acid without addition gave a corrosion loss on commercially pure iron of 0.02 and 0.06 grams. The corrosion loss for copper steel in the same acid shows respectively 0.04 and 0.088 grams loss, which is respectively 40 and 100 percent greater for the copper steel. Furthermore, the total corrosion loss with the addition of silver and copper salts in no case

[3] Chief Chemist, American Rolling Mill Co., Middletown, O.
[4] Chemical Engineer, The Institute of Industrial Research, Washington, D. C.

is as great with the commercially pure iron as with the copper steel. These results were obtained with dilute sulphuric acid about 0.10 percent strength.

O. P. WATTS (*Communicated*): Mr. Richardson says, "In some of their experiments they show no accelerated action," referring particularly to specimens 5, 6, 12 and 13.

In discussing 5 and 6 the authors had already pointed out in the paragraph immediately preceding Test II, that, where corrosion by the acid alone is very great, the accelerative action of the copper salt is but an insignificant part of the total corrosion, although the amount of corrosion by voltaic action is approximately the same as with the more dilute acid, but in a 1 1 cases where corrosion by the acid was slow, either because of its dilution, or because of the resistant nature of the metal, the accelerative effect of the copper or silver salt is unmistakably apparent.

Taken at their face value, Nos. 12 and 13 would seem to indicate that in normal sulphuric acid silver exerts a protective effect on ordinary low-carbon sheet steel; but this is contrary to its effect in all other cases. Where corrosion of iron by the acid is very rapid, the time during which voltaic action by the silver can take place must be limited, for the silver deposited must soon be undermined by solution of the iron, and, once detached, cannot again be deposited, for it is not appreciably attacked by the acid. The conditions for securing a reliable conclusion regarding voltaic action in the case of specimens 5, 6, 12 and 13 are then very unfavorable, and when specimens 12 and 13 run counter to experience with the 27 other specimens, it is probably best to register a verdict of "not proven" for these two.

Mr. Aupperle says that he does not believe the authors' conclusions are justified because no analyses are given. The conclusion stated in the sentence which ends immediately below Fig. 1, could perhaps be improved by inserting the adjective "commercial" before iron, so that it would read, "Voltaic action by copper and silver does stimulate corrosion of commercial iron and mild steel by sulphuric acid." While insertion of analyses of the three different materials tested would have added to the completeness of the paper, a knowledge of the exact composition of the particular

sheets of Armco iron or of Keystone copper steel can in no way alter the facts regarding the effect of a copper salt on their corrosion in sulphuric acid.

A comparison of the losses of specimens 38 and 42 shows that Mr. Coggeshall's sweeping statement that "the total corrosion loss with the addition of silver and copper salts in no case is as great with the commercially pure iron as with the copper steel," is not warranted.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

THE CORROSION OF OLD IRON[1]

By E. A. Richardson[2] and L. T. Richardson.[3]

Abstract.

Analyses are given of fifteen specimens of iron and steel which had been subjected to atmospheric corrosion for as much as 35 years. Five containing over 0.10 percent copper were all in good condition, five containing less than 0.10 percent copper were in fair to good condition, and five containing less than 0.10 percent copper were in poor condition; the results for over 0.10 percent of copper are conclusive, for less than this amount contradictory. A two-years' test, comparing old iron with recently made iron, showed that irons made several years ago are no more rust-resisting than those made today. [J. W. R.]

In reviewing the literature of the corrosion of iron and steel, numerous references are found dealing with old or moderately old specimens of iron or steel. Usually these specimens are ones that have apparently withstood corrosive influences; as a rule by the atmosphere. The literature relating to them usually consists of a description of the iron article, together with an analysis and sometimes with a photomicrograph showing the physical structure. Almost all of the examples of ancient iron have been found to be wrought irons. These have been reviewed in several places by others.

In a majority of cases little is known as to the methods of manufacture of these specimens of ancient iron, and the extent, intensity, and nature of the corroding influences to which they have been subjected can only be guessed. In some cases, a

[1] Manuscript received February 8, 1921.

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specimen of old iron may not be as rust-resisting as would appear at first sight. For instance, certain specimens of ancient iron from Egypt have showed marked corrosion when placed in the atmosphere of London. Other than a few such observations, we know of little work that has been done, so that, in general, it can be said that little is known as to the rust-resisting properties of ancient irons.

Recently, O. W. Storey published a paper on the corrosion of fence-wire, some of which was rust-resisting to the extent of having lasted 30 to 50 years. This article is perhaps the most comprehensive work that has been done on the rust-resisting properties of irons and steels that are known to have been subjected to corrosion. Roughly, Storey's work was done on fence-wire that had withstood corrosion in both acid and neutral atmospheres. His conclusion was that the rust-resisting properties of steel wire are due to a small amount of alloyed copper.

During the last five years the writers have been collecting and investigating specimens of iron and steel that have resisted corrosion for upwards of 30 years, and this present paper records the result of this investigation.

The specimens investigated were as follows:

1. Sheet iron from dome of old Wisconsin State Capitol Building. Exposed about 10 years. In fair condition.
2. Washer from same source. In good condition.
3. Nut from same source. In good condition.
4. Washer from same source. In good condition.

5 and 6. Two 1-inch (2.5 cm.) rods exposed to the weather at edge of lake for 30 years. Both in excellent condition. End of both rods threaded and threads still sharp as when cut.

7. Ax found lying on shore of lake at water's edge. In rather poor condition. Probably 35 years old.
8. Bolt from same source. In poor condition.
9. Pike-pole head from same source. In good condition.
10. *a.* Fence wire embedded 7 inches (18 cm.) in tree. In excellent condition.

    b. Another wire from same fence embedded in same tree 7 inches (18 cm.). In poor condition.
11. Nail used in fastening above wire to tree. In poor condition.

12. Wire exposed to atmosphere 30 years. In good condition.
13. Fence wire embedded in maple tree 6 inches (15 cm.). In good condition.
14. Fence wire embedded 4 inches (10 cm.) in oak tree. In poor condition.
15. Fence wire embedded 6 inches (15 cm.) in oak tree. In good condition.

Analyses were made of all of these specimens, particularly as to their manganese and copper content; the results are given in Table I.

TABLE I.

	S	C	P	Si	Mn	Cu
1. Sheet iron; dome Wisconsin State Capitol	0.006	0.01	0.111	0.079	tr.	0.007
2. Washer; dome Wisconsin State Capitol	0.006	0.06	0.092	0.17	0.37	0.15
3. Nut; dome Wisconsin State Capitol	0.006	....	0.42	0.10	tr.	0.081
4. Washer; dome Wisconsin State Capitol	0.011	0.02	0.32	0.08	0.012	0.005
5. Rod exposed to weather 30 years	0.006	0.005	0.214	0.252	0.03	0.38
6. Rod exposed to weather 30 years	0.020	0.01	0.102	0.062	0.03	0.05
7. Ax at edge of lake, 35 years old	0.007	0.005	0.274	0.29	0.06	0.05
8. Bolt at edge of lake, 35 years old	....	0.005	0.246	0.23	0.035	tr.
9. Pike pole 30 years old	0.015	....	0.100	0.003	tr.	0.02
10a. Fence wire 7 inches in tree. Good condition	....	....	....	....	0.66	0.18
10b. Fence wire 7 inches in tree. Poor condition	....	....	....	....	0.56	none
11. Nail in tree, same place. Poor condition	....	....	....	....	0.51	none
12. Wire 30 years old. Good condition	....	....	....	....	0.38	0.125
13. Wire 6 inches in maple tree. Good condition	....	....	....	....	0.45	0.13
14. Wire 4 inches in oak tree. Poor condition	....	....	....	....	0.37	0.01
15. Wire 6 inches in oak tree. Good condition	....	....	....	....	0.40	0.11

These results practically confirm those of Storey that steels which are rust-resisting contain copper, while those that do not contain copper are corroded rapidly.

In order to determine the relative rust-resistance of some of these old irons as compared to modern wrought iron, atmospheric exposure tests were made of the following specimens, covering a period of 24 months:

(a) Nut from dome of old Wisconsin State Capitol.

(b) No. 26 gauge sheet from dome of old Wisconsin State Capitol.

(c) No. 26 gauge charcoal iron, modern.

(d) Wrought iron pipe, modern.

(e) Wrought iron bar.

The loss in weight as determined before and after exposure was—

	Gms./cm.^{2}
Nut from dome of old Wisconsin Capitol	0.0746
26 gauge sheet dome of old Wisconsin Capitol	0.0920
Charcoal iron, modern—26 gauge	0.1049
Wrought iron pipe, modern	0.0708
Wrought iron bar	0.0667
Copper-bearing iron	0.0978
Copper-bearing steel	0.0490
Pure iron	0.1305
Open-hearth steel	0.1985

It is evident that irons made several years ago are no more rust-resisting than those made today.

DISCUSSION.

W. J. Beck[1]: This paper is very interesting. It is to be regretted, however, that the examples of old iron which have been referred to are all less than 35 years old, and the investigation is far from complete, as authentic data are not given as to the life of any of the specimens referred to.

In looking over the table of analyses on page 169, the highest sulphur content of any of the samples referred to amounted to but 0.02 percent, the average of the remainder being under 0.01 percent sulphur. The washer, sample No. 2, probably of Bessemer steel, as indicated by the remainder of the analysis, is

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shown to contain but 0.006 percent sulphur, whereas such steel should contain about ten times this amount. Sample No. 9, pike pole, which was said to be 30 years old, contains but a trace of copper (0.02 percent) and the authors refer to this low copper material as being in good condition. They also refer to a fence wire seven inches in tree, which contains no copper. The very fact that this material can be designated as fence wire at this time, although in poor condition, seems to indicate that the wire must have given fairly good service, as it was embedded to a greater depth in the tree than were three other wires, from which conclusions are drawn that they lasted a long time on account of the copper content.

In the olden days wire was galvanized without wiping, and consequently had a heavier zinc coating than modern wire. The benefits of the galvanizing have been ignored by the authors. Some of the wire in poor condition may not have been galvanized, while that in good condition may have been galvanized.

L. T. Richardson: In a general way the majority of the pieces show that the samples containing copper were in better condition than the ones which contained no copper.

Colin G. Fink[2]: I would like to ask Mr. Richardson whether he looked for any other elements besides copper? I mean elements such as nickel, for instance, or chromium, or did he go right after copper and more or less assume that it must be the copper, and ignore the other elements?

L. T. Richardson: I am not absolutely sure. My brother made these analyses, and, as I remember, he has made some analyses for nickel and chromium, but whether they were in this particular set of materials I do not know.

Colin G. Fink: Because it may very well be that a small percentage of, chromium say, would have a similar effect to that of copper.

J. W. Richards[3]: Dr. Fink, I may say that I am responsible and not Mr. Richardson, in making that abstract. I noticed some contradictions in those steels containing less than 0.1

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percent copper. Some of them which contained very little copper in that range were in good condition, and others containing nearly up to one-tenth were in bad condition, and so I wrote the abstract. I would like this abstract to be revised by Mr. Richardson, if he doesn't agree with it, because I wrote it independently of him. The five specimens containing over 0.1 percent of copper were in good condition. The ten specimens containing less than 0.1 per cent of copper—half of those were in fair to good condition, and half of them in poor condition—so that there are no conclusions to be drawn for specimens of less than 0.1 percent copper. Only conclusions can be drawn in specimens of over 0.1 percent copper—they were all in good condition.

A. S. Cushman[4]: I have analyzed a great many samples of fence wire, running over 15 years, and investigations taken at random on observation trips in different parts of the country, selecting good and bad wires of fences, and I haven't been able to find out that copper content had anything to do with it, because nearly all wires, good and bad, didn't have any copper to amount to anything. It is a rare thing to ever find a copper content in the fence wires, because copper has not been used by the manufacturers of wire purposely to confer rust resistance,

O. W. Storey[5] (*Communicated*): This paper again confirms the mass of data which show that copper is of much value in lessening corrosion. I was especially interested in the data obtained from the fence wires in which the wires containing copper were in good condition, while those low in copper were in decidedly poor condition. These results confirm those which I have obtained covering analyses of about 80 different fence wires. In these 80 different wires, in every case without exception, where the wires were subjected to identical conditions, the wires which were in better shape always contained copper. It is indeed fortunate that the barb wire industry of 30 to 50 years ago furnished barbed wire containing several varieties of steel which could not help but be corroded under identical conditions. The corrosion of these wires over a long period of years justifies the

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[5] Metallurgical Engineer, C. F. Burgess Labs., Madison, Wis.

conclusions reached during the past 10 years by experimenters who have obtained results covering much shorter periods of time.

E. A. RICHARDSON (*Communicated*): Mr. Beck's remark as to the incompleteness of the data is very true. However, it is almost impossible to obtain complete data on such specimens as are described in this paper; this is regrettable.

The amount of sulphur in washer No. 2 should be 0.060 as indicated by Mr. Beck.

It is very unlikely that we have compared galvanized with ungalvanized wire. We have been told that uncoated wire was almost universally used in the locality from which these specimens were obtained.

In answer to Dr. Fink's question, all of the rust-resisting specimens were tested for nickel and chromium and some for vanadium. None of these elements was found. Corrosion tests have shown that small amounts of these elements have no great effect on the corrosion of iron.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

THE CORROSION OF STEEL RANGES.[1]

By Oliver W. Storey.[2]

Abstract.

The modern kitchen range is studied from the standpoint of the cause of corrosion to the steel in its various parts, and the seriousness of the corrosion. Experiments were made with copper-bearing and "Armco" sheet at points where corrosion was greatest, showing that the more copper contained in the sheet steel the less the corrosion. The economic importance of further researches in this line is pointed out. [J. W. R.]

Corrosion is the chief agent of destruction in a steel range burning coal or wood. In a gas range the corrosion is much less severe, though it sometimes limits the life of the range. The mitigation or prevention of this corrosion is a most important problem to this industry whose output amounts to many millions of dollars per year. This corrosion probably directly affects a majority of the families in this country, and is of much importance to them, since the present-day steel range costs from 125 to 200 dollars, while a gas range costs from 35 to 125 dollars. Such an investment must be justified by a reasonable length of service.

The construction of a range will be sketched briefly to secure a better understanding of the problems involved. In describing the range throughout this paper the observer will assume that he is looking at it from the front or oven-door side.

A range consists essentially of a central oven surrounded by flues on all sides except the front, where the oven door is placed, and at the left where the firebox is. The construction is such that the products of combustion travel to the right over the top

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of the oven, down the right side, and underneath the oven and out into the flue at the rear. A baffle under the oven directs the gases to the front before they finally pass to the rear and into the back flue. This is deemed necessary to secure a more even temperature in the oven. The construction must be such that the heat may be utilized at the following points: in the oven, on the top of the stove, and in an optional water reservoir at the right end. Except for the stove top the outside walls of the flues are insulated.

The products of combustion, after leaving the firebox, first come in contact with the stove top and the top of the oven. The stove top is made either of cast or malleable iron and is often heated to a low red with a hot fire. The top of the stove lids and cross frames are often subjected to the action of various liquids, which may be spilled from time to time, combined with the scaling action of the high temperatures. The under side of the lids are subjected principally to the scaling action of heat and only slightly to corrosion by products of combustion.

The oven body is usually made of a single thickness of sheet steel. The top of the oven is subjected to the intense action of heat and the products of combustion as they leave the firebox. In addition, garbage is often burned here and liquids spilled on the stove may find their way to the oven top. The corrosion of the steel at this point is principally that due to direct oxidation.

After traveling over the oven the gases of combustion pass down the right side and under it. As the temperature of the gases drops steadily, the direct oxidation of the steel decreases. From the bottom of the oven the gases pass into the back flue which is subjected to intense corrosion, especially when a stove is used intermittently. Here the oxidation due to the heat is almost negligible. Moisture, tar acids, sulphurous acid, soot and the other products of combustion are condensed and settle here and are usually highly destructive.

Present-day steel ranges have an outside wall of sheet steel. To provide proper insulation a layer of asbestos is usually placed on the inside of this sheet steel. In some designs a cast iron grating holds the asbestos in place, forming the flue wall, and allowing the asbestos to be exposed to the products of combustion. In others a sheet-steel lining is used to support the asbestos.

The presence of the asbestos introduces a new complication. When the range cools, the asbestos absorbs moisture from the atmosphere. When again heated, it "sweats" and moisture is deposited on the cool sheet steel next to it. Corroding agents absorbed from the flue gases are doubtless also present in the asbestos and these are probably driven along with the moisture. This condition often results in the rapid corrosion of the outside wall of the stove and is one of the chief difficulties the range manufacturer must overcome. This destructive action comes at a place where it is immediately evident to the housewife because it spoils the appearance of the range. The damage also makes repair or replacement necessary, as it impairs the efficiency of the range.

As may be expected, the interior of the oven also corrodes. This is not a serious problem from the corrosion standpoint, although it is serious to the housewife who objects to a rusty oven. Often the rear flue, where there is rapid corrosion, rusts out completely and corrodes through the rear wall of the oven. When a range is used continuously the corrosion is lessened considerably. On the other hand, if a new fire is kindled every morning, or before every meal, the conditions are at their worst.

Corrosion in a range also takes place to a marked degree when not in actual use rather than when heated to its maximum temperature. This corrosion is not only present in solid fuel ranges, but may also be seen in gas ranges. Ranges and other steel construction used in connection with products of combustion, are usually subject to more active damage when not in use than when in service, and like many pieces of machinery, disuse or irregular use causes more deterioration than continual use under good care.

The influence of a cool surface is seen in the back flue, which usually corrodes rapidly. When the fire is extinguished, the flue cools rapidly as it is exposed to the surrounding cool atmosphere. The sooty deposit attracts and holds moisture, instead of acting as a protection. Not alone is the moisture from the atmosphere absorbed, but moisture from the burning fuels is condensed here. This moisture absorbs carbon dioxide, sulphurous acid, and tar acids, forming an intensive corroding medium. With a slow fire and low flue-gas temperatures this condensation and corrosion may occur while the stove actually is in use.

Therefore an important principle of design to be followed is to secure uniformity of temperature as far as possible by avoiding parts particularly exposed to cooling influences. This may be accomplished in various ways, including the insulation of either side of that portion of the structure most exposed to external cooling influences. Experimental work has clearly demonstrated that there is marked corrosion especially at points that stay relatively cool when a stove is in use, due to the condensation of moisture at such points. This also is important in the construction of gas-range ovens.

The manufacturer may avoid much trouble by shunning certain localities, as it has been found that the steel in ranges corrodes much more rapidly in certain sections. This variation of corrosion is usually caused by the variation of local fuels used.

The high sulphur fuels, such as certain Illinois bituminous coals, are often the cause of rapid corrosion. In general the Western bituminous coals are more destructive than the Eastern coals. Some of the lignite coals of North Dakota also cause rapid corrosion. The products of combustion resulting when corn cobs are used as a fuel are especially corrosive. The xylan of the corn cob when destructively distilled, yields furfural, which in turn may oxidize to pyromucic, acetic and possibly formic acid. In certain portions of Texas the steel in ranges corrodes rapidly. The use of mesquite as a fuel is the cause of the difficulty since the products of combustion of mesquite are similar to those from corn cobs. The corrosion is accentuated in the region contiguous to the Gulf of Mexico where the atmosphere is moist and salt-laden. On the other hand it is only in very dry climates like those of Oklahoma, New Mexico, and Arizona, that practically no damage from corrosion results.

Various methods are used to prevent corrosion. The cast or malleable-iron stove tops are subjected to various processes. Protective coatings having organic compounds for a base are useless, as these soon burn off. The writer's tests of the phosphate treatment, which has given excellent results under many conditions, indicate that it does not give lasting results when used on stove tops. The oil application soon burns off, leaving a porous coating that breaks down rapidly especially when liquids are spilled upon it. The most successful treatment is the magnetic oxide,

or Bauer-Barff process, modified to suit the conditions. This oxide coating, when properly applied, stands up under harsh treatment even at a low red heat.

The corrosion on the under side of the stove top is negligible as is the case of all malleable or cast iron used in stove construction. It is not of importance, since the housewife is chiefly concerned with the upper side, which should retain a smooth black finish to conform to the pleasing appearance of the other portions of present-day ranges. A rusty and pitted range top may result if the top is not protected properly. It must be understood that a range with its white enameled sections and simple but artistic trimmings, is now regarded by the housewife as a necessary piece of equipment, which is also an ornament to her kitchen.

A few of the many methods used for overcoming corrosion in the body of the stove will be discussed. Cast or malleable parts are sometimes substituted for sheet steel in highly corrosive situations, though this method has obvious objections, such as difficulty in making suitable castings, weight of such castings, and poor appearance. It seems to be almost necessary, for the sake of appearance, to use sheet steel having the familiar blue-gray Wellsville finish for the outside wall of the range. The use of vitreous enameled sheets for this purpose is increasing rapidly though the cost is increased considerably. The vitreous enamel is applied to both sides and therefore has the advantage of permanently protecting the outside wall of the range against the corrosion due to "sweating" of the insulating asbestos.

In one construction sheet copper is placed between the outside wall and the asbestos, the construction being such that an air space is left between the copper and the steel. The copper is used since it is supposed to be non-corrosive and "does not rust." Nevertheless, since the asbestos is a poor insulator, the copper becomes hot enough to scale, especially in certain less favored sections of the range. While the copper resists corrosion at ordinary temperatures, its use under the above conditions has shown it in actual service to corrode readily when a high temperature is combined with the products of combustion.

The use of special sheet irons and steels in the construction of ranges, especially for those parts subjected to the action of flue gases, has been tried with better results. One manufacturer uses

steel flashed with a copper deposit which is of doubtful value. Another uses a so-called aluminum-coated steel, the "aluminum" being principally zinc. When this coating is subjected to the products of combustion in flues it does not withstand these conditions any better than ordinary steel. It probably has merit when used in oven interiors. Along this line, a gas-stove manufacturer has recently used sherardized steel for the oven interior. This is applicable to steel-range ovens. The protective methods usually must vary since at one point the flue is subjected to intense heat and direct oxidation, while at another point the corrosion is due to moisture and corrosive gases.

A method, which apparently is giving good results, is to line the flues with a sheet steel coated with a vitreous enamel. With this construction the oven is given a double wall due to the difficulties in making an oven having a single thickness of enameled steel. The steel must be shaped before being enameled. A special construction overcomes the chipping of the enamel when it is riveted into place. The vitreous enamel has the excellent property of withstanding the high temperatures at the top of the oven, thus preventing oxidation, and it also is impervious to moisture and the products of combustion, making it ideal for protecting the back flue.

During the past ten years the C. F. Burgess Laboratories have been studying the steel range corrosion problems, especially those connected with the corrosion of the sheet steel. After the preliminary experimental work demonstrated the causes of corrosion in the various parts of a range, a survey was made of the steels available for range construction. The researches of C. F. Burgess[3] and D. M. Buck[4] on the addition of copper to iron and steel had just been published when this work was started and it was assumed that steels resistant to atmospheric corrosion would be more resistant also to the flue gases in ranges. American "Ingot" (Armco) iron and charcoal iron, both regarded then as highly resistant to corrosion, were included in the survey, and all of these compared to the ordinary steel. Various protective methods were tested also.

The specimens, in the form of sheets about 3 x 5 inches (7.5 x

[3] Burgess, C. F., and Aston, J.: Influence of Various Elements on the Corrodibility of Iron. Trans. Am. Electrochem. Soc. (1912), 22. 241.

[4] Buck, D. M.: Jour. Ind. and Eng. Chem., June, 1913

12.5 cm.) were mounted in the flues of stoves in actual use in households in different sections of the country. However, most of the specimens were sent to that portion of Texas next to the seacoast, where there is rapid corrosion. Great care was used in placing the specimens in the flues so that reliable results were obtained. After some experimenting a satisfactory method was found. The specimens were allowed to corrode from a few months to several years, and the corrosion over long and short periods of time studied. All specimens were carefully cleaned and weighed before and after corroding, the rust being removed by the ammonium citrate method.

The first results showing the relative merits of the materials then used in range construction follow:

1. Under these severe conditions a copper steel (Keystone) is much more resistant than ordinary Bessemer steel, charcoal iron, or American "Ingot" iron. There is little difference between the last three, though the Bessemer steel generally is the poorest.

2. The Bauer-Barff coating is very resistant under severe conditions.

These results have been repeatedly confirmed in later tests.

A study of all available data resulted in the conviction that the use of a steel highly resistant to corrosion would probably be the solution of many corrosion difficulties in a steel range, although other forms of protection would have to be used in conjunction with it. It was also recognized that the oxidizing influences of high temperatures would probably require a different steel than one subject to lower temperatures and corrosive gases.

The results made it evident that the data obtained in atmospheric corrosion tests could not be directly applied to the corrosion by flue gases. The encouraging results obtained with the Keystone steel containing 0.25 percent of copper suggested the making of steels containing larger amounts of copper. Sheets containing copper up to one percent were made and later sheets containing over 2 percent.

The results were surprising. Instead of showing but a slight increase in resistance to corrosion as under atmospheric conditions the increase in resistance was a straight line function of the copper percentage. In other words, the high copper steels were

much more resistant than the low copper steels to the conditions in the back flues of ranges. The quantitative data following are taken from a patent[5] based on the results obtained with the high-copper steels. The losses are given in grams for equal areas of surface and each loss represents the average of several sheets. The several sheets of each series checked closely.

No.	C	Mn	S	P	Cu	Average Loss
1 ("Ingot Iron).....	0.02	0.05	0.030	0.008	0.06	37.98
2 " "	0.05	0.05	0.036	0.004	0.07	39.52
3 (Keystone).....	0.12	0.42	0.041	0.063	0.24	26.10
4	0.10	0.47	0.043	0.018	0.572	20.75
5	0.11	0.45	0.032	0.010	0.950	14.41
6	0.12	0.46	0.047	0.014	1.118	13.56

These data show the relative superiority of the ordinary copper-bearing steel (Keystone) over American "Ingot" iron under the highly corrosive conditions in the back flues of a range. The work along these lines is continuing, the alloying metal not being confined to copper.

The data obtained in this research on the corrosion resistance of alloys used in steel ranges may be applied to many other situations where there are similar conditions. The ordinary gas range is subject to similar corrosion, but in a mild form. There are many places where the corrosion due to the products of combustion is a serious factor. As an example, steel smoke-stacks and the stovepipe used in dwellings are corroded rapidly.

CONCLUSIONS

From the results obtained in this work it is apparent that the corrosion data obtained in atmospheric tests cannot be applied to the conditions present in ranges. A steel range presents a multiplicity of problems in corrosion and the results obtained at one point cannot be applied to other parts of the range. Each portion of the range requires a separate study for the elimination of corrosion which is the chief factor in its ultimate destruction.

[5] Silas McClure, U. S. Patent 1,341,992, June 1, 1920. Corrosion-resisting Ferrous Alloy.

It has been shown that high-copper steels are especially resistant to the combined action of the products of combustion, and the alternate heating and cooling of a range. The results obtained under these conditions should be applicable to other situations where there are similar conditions.

The indications also are that the ultimate solution of the problem lies in the use of alloy steels or possibly other alloys, combined with protective methods such as Bauer-Barffing and vitreous enameling and by improvements in design. The use of an alloy costing considerably more than plain steel is justified at certain places in a range where there is excessive corrosion. This field, which has been almost untouched by investigators, should offer many possibilities to ferrous and non-ferrous alloys.

The writer wishes to thank Mr. Silas McClure, of Beaver Dam, Wisconsin, at whose request this research is being undertaken, for his valuable assistance in the preparation of this paper.

C. F. Burgess Laboratories,
January 26, 1921.

DISCUSSION.

J. A. Aupperle[1]: The subject, "The Corrosion of Steel Ranges," which Mr. Storey has studied, is a very important economic problem. The company I represent manufactures many grades of sheet metal, among them being copper-bearing steel. Our research work has been along the lines of furnishing the metal best suited for each specific purpose; we are, therefore, not committed to the manufacture of one kind of metal for all purposes. We furnish pure iron to more than two hundred manufacturers of stoves, ranges and furnaces. If the trade wants an alloy for ranges we will be glad to co-operate in making tests in order to determine whether it is desirable to substitute an alloy for pure iron. We can not accept such claims as Mr. Storey presents for copper-bearing steel used in steel ranges, as his data are far from conclusive.

Mr. Storey has referred to the corrosion in the back flue, especially when the stove is used intermittently, and says that the

[1] Chief Chemist, The American Rolling Mill Co., Middletown, Ohio.

oxidation at this point is almost negligible. Still, he condemns pure copper on account of scaling at high temperatures, while the pure copper undoubtedly would have given the best results in the flue test. Mounting small samples in the flues where relatively low temperatures prevail, therefore, yield no information as to the life of sheet metal which is also subjected to high temperatures in ranges.

We are in accord with Mr. Storey's statement that pure copper, on account of the tendency of pure copper to scale at high temperatures, corrodes quite readily when subjected to high temperatures in combination with the products of combustion. We have also found this tendency of copper when alloyed with ferrous metals to accelerate the rate of corrosion.

We have conducted tests on 16-gauge samples of iron and steel which were first pickled and then placed in an electric furnace and heated to a temperature of 800° C. Our tests have shown that copper-bearing steel corrodes about eight times as fast as pure iron made in open-hearth furnaces. The following table shows the number of hours it required for the failure of such metal:

Material	*Hours Heated*	*Si*	*S*	*P*	*C*	*Mn*	*Cu*
Pure Open-Hearth Iron ..	645.0	trace	0.025	0.008	0.008	0.018	0.020
Copper-Bearing Steel	72.5	—	0.038	0.010	0.090	0.444	0.281

We concur with Mr. Storey's statement that the Bower-Barff Process, which consists of coating the sheet metal with magnetic oxide of iron is very efficient in preventing corrosion under the conditions which exist in ranges. We believe that the greater durability of pure iron over copper-bearing steel, when subjected to the action of high temperatures, is due to the fact that the magnetic oxide of iron formed is cemented to the pure iron; whereas, in the case of steel this magnetic oxide is continually detached from the base metal, which fact can be accounted for by the escape of gases that have been occluded by the steel.

L. Baraduc Miller, in the 1914 "Carnegie Scholarship Memoirs of the British Iron and Steel Institute," refers to the gas content of Bessemer steel, and has shown that when allowed to cool in a vacuum that 75 cubic feet of gas per ton of steel was liberated from the vacuum-treated metal. These gases consisted chiefly of hydrogen, carbon monoxide and nitrogen.

Austin, in the "Journal of the Iron and Steel Institute," 1912, published his experiments where he took cold open-hearth steel which he electrically melted in a vacuum, and collected the evolved gas. This open-hearth steel evolved the equivalent of 35 cubic feet of gas per ton of metal, and in another instance 47 cubic feet of gas per ton of metal was evolved from another sample of open-hearth steel.

The gases, having a tendency to escape from the sheet metal, especially when heated, would have the effect of loosening the magnetic oxide of iron formed on the copper-bearing steel sheet, and thus expose fresh metal to corrosive attack. This is an important point that has been entirely ignored in Mr. Storey's experiments.

Reference has also been made to the corrosion of sheet metal in contact with asbestos, on account of sweating. The condensation products would undoubtedly carry sulphuric acid, which would form ferrous and ferric sulphate in contact with the metal.

Reference has been made to the use of steel for ranges, that has been flashed with a copper deposit, which Mr. Storey believes is of doubtful value. I have confirmed what Mr. Storey says, and instead of being only of doubtful value, we find copper in contact with steel to be deleterious from a corrosion standpoint, when such metals are subjected to the action of ferrous and ferric sulphate as found in steel ranges.[3]

In Mr. Storey's experiments, 3 x 5 inch samples were mounted in flues of stoves where the temperature was too low to scale the metals and the samples remained from a few months to several years. It would be interesting to know whether Mr. Storey has attempted to average the losses obtained in short periods with those obtained from long periods in arriving at the quantitative data which he has submitted.

On page 182, Mr. Storey refers to quantitative data from a patent issued to Silas McClure. Mr. Storey credited this data to Silas McClure's patent. I should like, therefore, to know by what code of ethics Mr. Storey has interpolated into this table the words "Ingot Iron" and "Keystone," as neither of these metals are mentioned in the original patent referred to. Mr.

Strickland. American Electrochemical Society, 1921, **39**, 123.

[3] Observations on the Corrosion of Iron and Steel. By J. A. Aupperle and D. M.

Storey then refers to the data and interpolates another word, by referring to American "Ingot" iron, which also has not appeared in the table.

In the above-mentioned table the carbon and manganese contents are from 2 to 4 times higher than the percentage of these elements ordinarily found in normal pure iron made in open-hearth furnaces.

We have made tests on pure iron, plain steel and copper-bearing steel, by constructing a drum of each of the different kinds of metal and mounting on this drum, stove pipes made from the three kinds of metal. The position of each metal varied in each stove. The drum and top section of each stove was made from the same kind of metal. These stoves were fired with soft coal once a week, and the remainder of the week the stoves were opened so that air could circulate through each stove. At the conclusion of the test we found that copper-bearing steel was in the worst condition, whether it was used in the body of the stove or in the first, the second or the third section of the stove pipes.

Mr. Storey has shown that pure copper will not withstand the combined action of high temperatures and products of combustion. Since Mr. Storey has condemned the use of copper for ovens, it would be interesting to know whether he tested metallic copper in flues where low temperatures prevail, and, if he did, whether the copper did not withstand corrosion in the flue better than ferrous metals. This information would have an important bearing upon his conclusions, as he condemned the use of metallic copper for ovens; whereas the metallic copper would undoubtedly have been the best metal, based upon the tests made in the flues.

J. W. Richards[4]: On the last page of his conclusions Mr. Storey speaks of protective methods, such as the bare finish. Now that is oxidizing of metal and forming a protective magnetic coating on it, and under those conditions copper-bearing steel will give a better bare finish or protective coating than a copper-free steel.

[4] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa

H. L. KOHLBERG[5] (*Communicated*): The article on the corrosion of steel ranges, by Oliver W. Storey, points to the very interesting fact that the more copper there is contained in the steel subject to corrosion in the flues of the range, the less is the actual corrosion sustained.

Conditions not very dissimilar to those obtaining in the flue of steel kitchen ranges are present also in the flue and breeching of steam boilers, dampers and stacks. It would, therefore, appear that the same remedy, copper-bearing steel having two percent or more of copper, would apply for this sheet steel work as well.

Table II on page 148, by Mr. F. N. Speller, on preventing corrosion of iron and steel where not exposed directly to the atmosphere, seems to show that copper-bearing steel does not have any influence in preventing the corrosion in hot water pipes.

For the purpose of this discussion, I assume that the steel used in these experiments carried only one-fourth of one percent copper, similar to the usual copper-bearing steel. Has steel, carrying upwards of two percent copper, ever been tried for hot water pipes or similar uses?

O. W. STOREY (*Communicated*): With reference to Mr. Aupperle's discussion, I wish to say that my paper records the results of ten years of experimental work in the attempt to make sheet steel ranges more resistant to corrosion. Furthermore, these experiments were carried out in ranges in everyday use in homes, representing conditions that would be met generally. Therefore the data and conclusions given in this paper are not the deductions of theoretical considerations or laboratory experiments such as Mr. Aupperle apparently bases his conclusions upon.

Mr. Aupperle intimates that metallic copper would corrode slowly in the back flues of ranges where the temperature is comparatively low. Experience shows that copper corrodes rapidly here and should not be used. While the temperature is low enough to practically prevent any scaling action of iron or steel, it is still high enough to cause copper to oxidize readily. This oxidation, when combined with the corrosive action of the products of combustion, destroys the copper rapidly. When the

[5] Mechanical Engineer, Warren, Ariz.

range is run "hot" the temperature is high enough to cause rapid scaling of copper.

Mr. Aupperle states, "Mounting small samples in the flues where relatively low temperatures prevail, therefore yield no information as to the life of sheet metal which is also subjected to high temperatures in ranges." This is followed by a table giving the comparative losses of pure iron and copper-bearing steel when heated at 800° C. I was careful in my paper to point out that the results obtained at one point in a range cannot be applied to another where other conditions prevail and make no such claims as are inferred by the above quotation. Some work has been done on the corrosion of steel at points in the range where scaling temperatures often occur, but these results do not show any superiority of Ingot Iron over copper-bearing steel. On the contrary, the results, though not uniform, tended to show a slight superiority for the copper-bearing steel. The table presented by Mr. Aupperle does not have any bearing on the controversy, since such temperatures as 800° C. are not encountered except in the firebox and unprotected steel is not used where excessive scaling may occur. The steel is enameled or another construction of cast or malleable iron is used. Mr. Aupperle's tests, in addition to using a temperature several hundred degrees above those obtained in a range, were carried out in the pure atmosphere of an electric furnace, whereas the conditions are entirely different in a range. His experiments therefore have only a remote application to range construction, and many references are cited to show why the magnetic oxide should adhere less tenaciously to copper-bearing steel, but under conditions in a range the large number of other factors encountered entirely overshadow the effect of the gases present in the steel. While the presence of the gas in the steel was probably ignored in my experiments, the results of the experiments show that this can be done safely.

Mr. Aupperle asks about the relation of the tests covering a short and long period of time. The results indicate that the efficiency of the copper-bearing steel is more pronounced over a long period of time.

A reference is made to the corrosion of copper-bearing steel in the presence of ferrous and ferric sulphates in a water solution,

and it is intimated that these results probably apply to the corrosion in ranges. Here again Mr. Aupperle tries to apply laboratory results to service conditions. The two conditions are so dissimilar that there is apparently no basis for his attempts to apply the results of his tests to range conditions.

With reference to Mr. Kohlberg's inquiry about the use of high copper steel in flues and stasks of steam boilers, I believe that such high copper steel can be successfully used at these points, providing the conditions are similar to those obtained in the flues of kitchen ranges. I believe high copper steel would give excellent service under these conditions.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

UNUSUAL BOILER TUBE CORROSION BY CARBON DIOXIDE.[1]

By Barzillai G. Worth.[2]

Abstract.

A steam boiler corroded rapidly, and resisted all attempts to protect it electrolytically. Finally the trouble was located as due to soluble iron bi-carbonate in the water used, which gave off large quantities of carbonic acid gas when heated in the boiler. The water was then treated by being kept at the boiling point eight hours in a pre-heater, where the carbonic acid gas was liberated and a sludge of ferric hydroxide precipitated. The trouble then ceased. [J. W. R.]

The destruction of feed-water piping and corrosion of boiler tubes by dissolved carbon dioxide is a well-known occurrence, but the following unusual case of boiler tube corrosion may be of interest as showing how unusual feed-water impurities in some localities can accentuate this condition, and require special means to obtain satisfactory feed-water conditions.

The boiler in question is located in a plant at Keyport, N. J. It is of 264 H.P. (A. S. M. E.) rating, Babcock & Wilcox make, longitudinal drum type, with cast-iron vertical headers and No. 10-gauge hot-finished seamless steel tubes. The boiler when first installed was fitted with hand-fired grates, but on account of labor conditions the boiler was later equipped with a Reagan overfeed stoker, burning run-of-mine bituminous coal under moderate forced draft. The tubes are cleaned by hand-operated lance blowers. The boiler was normally operated at 150 lb. pressure per sq. in. (10 atmospheres) and 125° F. (70° C.) superheat, supply-

[1] Manuscript received March 22, 1921.

[2] Vice-Pres. Walter Kidde & Co., Inc., Engineers and Constructors, New York City.

ing steam to a turbo-generator furnishing current for an electrochemical plant, and the load was very uniform. Except for periodical shut-downs, this load was on for 24 hours per day seven days per week.

The feed water for the boiler was taken from a creek which comes down through the Jersey mud hills of this section and is dammed up at the plant to produce a pond, just before it flows into Raritan Bay. This pond has a water level only a few feet above mean high sea-level. In the summer and autumn this water is quite full of vegetable material. Sometimes in the winter a high tide backs up over the weir and floods the reservoir with salt water.

Analysis of the water varies, an average sample being about as follows:

	Grains per U. S. gallon	Mg. per liter
Silica and clay	0.373	6.42
Iron and aluminum oxides	0.257	4.42
Sodium chloride	0.560	9.63
Calcium sulphate	1.563	26.88
Magnesium sulphate	0.910	15.65
Organic matter	0.326	5.61
Total solids	3.989	68.61
Free sulphuric acid	0.592	10.18

It will be noted that this analysis is not by ions, as employed by the U. S. Geologic Survey, for this method of stating analysis, though preferable, was not employed in this case until the plant laboratory took up the matter.

The condensate from the turbine was returned to the boiler, and the condensate from a considerable manufacturing load in the form of heating coils also returned to the boiler. However, there were also a number of heating operations which were performed by passing steam directly into the solutions, and a large amount of distilled water was used for factory purposes, so the boiler make-up amounted to about one-third of the total evaporation.

The creek water before going to the boiler was treated in a standard lime and soda softener with the usual chemical feed apparatus, sedimentation tank, and filter. This softener had a capacity of approximately 8,000 lb. (3637 kg.) of water per hour,

which is ample. The treatment was designed to take care of the scale-forming material and acid. Salt water was handled by salinometer tests and blowing down.

For the first few years, and before installing the stoker, the boiler was operated at about 125 percent of rating without special difficulty, but after the stoker was put in and the load increased to approximately 175 percent of rating, with correspondingly increased demands on the water softener, tube failures began to be experienced and soon became serious.

These failures were due to pitting and perforation of the tubes. The pits at first were small hemispherical spots and would break out in tiny holes which could be permitted to go without repair for weeks without seriously affecting operation. But soon they were no longer small holes, but areas of 0.5 to 1.5 inches (1.3 to 3.8 cm.) in diameter would be corroded down to paper thinness, and then this area would open out and the boiler could not carry load and maintain pressure. The drums were also slightly pitted, the pits being of an irregular shape and very shallow.

In two cases the holes in the tubes were so large that the water ran out as fast as feed pumps could force it in, feed was cold, pressure dropped, pumps had to stop for want of steam, boiler drained out down to hole in tube, and in spite of drawn fire the hot setting heated the tubes and racked the boiler to such an extent that every tube in the boiler had to be re-expanded and tightened.

The location of pitting in the drums was almost entirely at or near the rear ends, where the feed water was discharged into the boiler. The pits in the tubes were almost entirely in the lower or rear section where the relatively cool water was being heated as it came from the downflow header. All the holes were in the tops of the tubes.

This pitting was at first assumed to be due to carbonic acid gas generated from the vegetable material in the water, and special pains were taken to filter this vegetable matter out and to increase the effectiveness of treatment. In order to get more dependable results, instead of using lime and soda-ash, caustic soda was introduced directly into the water, thus eliminating the lime salts introduced by the lime soda treatment. This helped somewhat, and the feed-water softness was very much more uniform, but it was still insufficient to stop the pitting.

Next the introduction of zinc plates was tried. Two plates were placed in each drum, entirely submerged and carefully connected electrically with ⅞-inch (2.2 cm.) iron rod tapped into plates and into the top of shell of drum. The effectiveness of the zinc plates was measured by carefully mapping and measuring the pits in the drum. The pitting of the tubes was inaccessible and thus could not be measured. The zinc was quite effective in preventing the further pitting of the drum, but the trouble in the tubes continued to be apparently as bad as ever. Apparently the

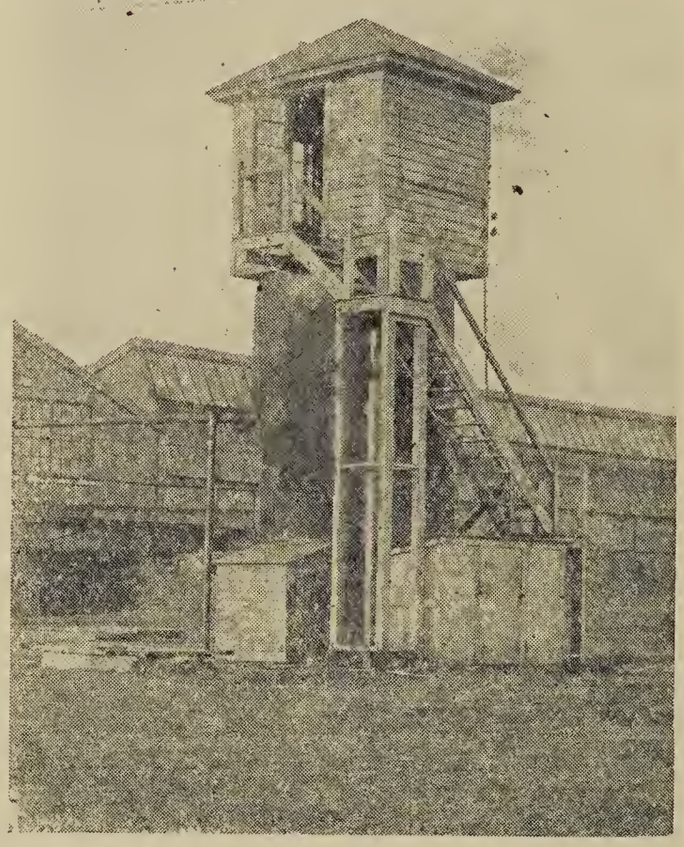


FIG. 1. Water Softener.

galvanic currents from the zinc did not penetrate down the headers and into the tubes to any extent. At this stage the use of electrolytic protection or cathodizing was carefully considered, this protection having been used very effectively in this plant for the protection of cell parts, etc. But it was considered at the time that since the zinc showed such poor results, it was better not to attempt it.

A careful laboratory study of the condition of the water was made by the chemist in charge of the electrochemical plant. This

study brought to light a condition previously unnoticed in the feed-water analysis and design of softening system, *i. e.*, that one of the important impurities of this water was a soluble bicarbonate of iron, $H_2Fe(CO_3)_2$. This compound is characteristic of all the water in this section, well-water as well as surface waters. This bicarbonate of iron remains stable at ordinary temperatures, but when heated breaks up rapidly with release of carbonic acid gas, the precipitate being a ferric hydroxide which colors red all scale and mud. Although the softening treatment

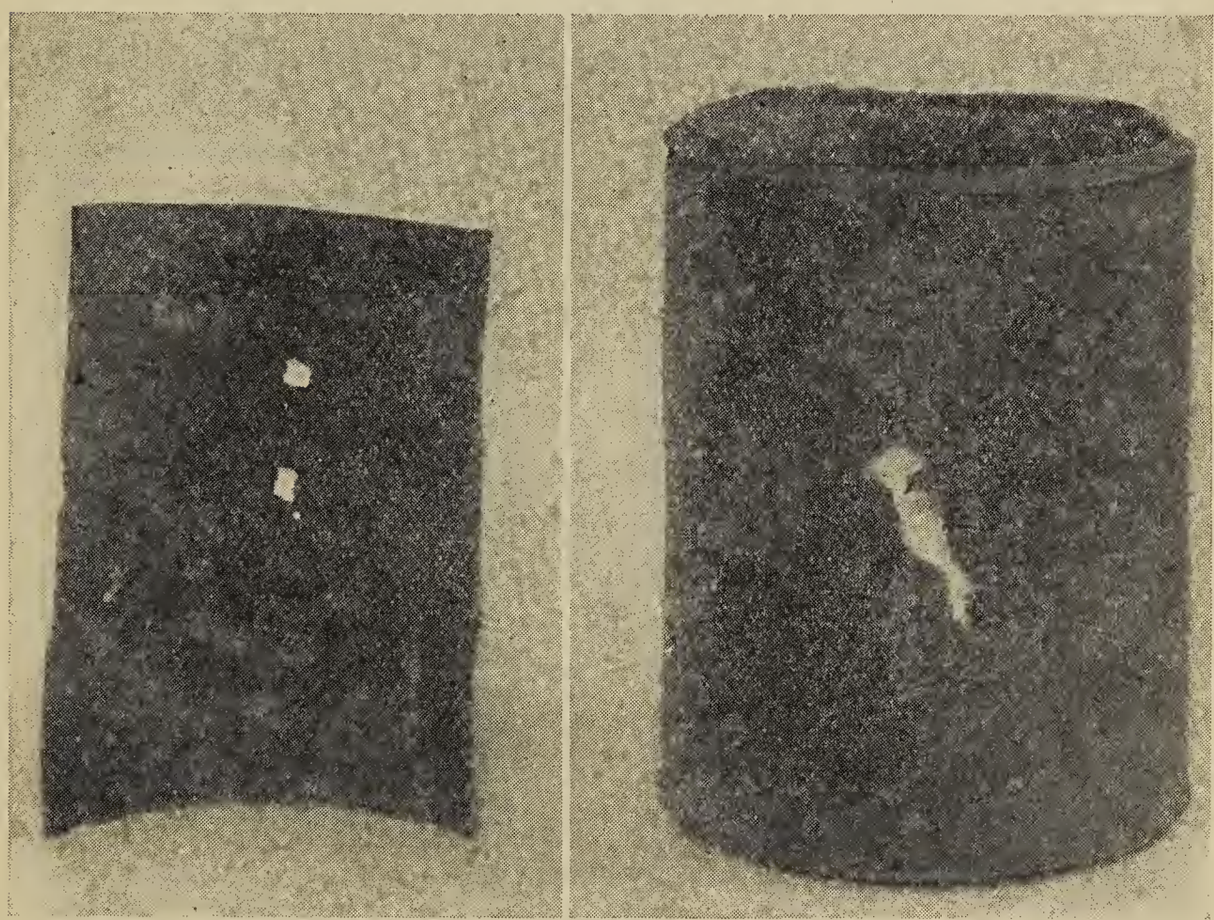


Fig. 2. Ruptured Tube.

should under ordinary circumstances have taken care of this, a considerable amount of bicarbonate was fed into the boiler in spite of the treatment. This was due to conditions in the creek, where the changing water composition every few hours, due to rains and other conditions, made it impossible to maintain an exact adjustment of the chemical softening treatment, and thus bicarbonate was frequently carried into the boiler.

The consequence was that when the feed-water entered the boiler and was heated to high temperature carbon dioxide was

given off in large quantities, and this was probably responsible for the rapid corrosion. Where the feed-water entered the drums at the rear ends from the feed line it was comparatively cool and the corrosive effect small, but where the water entered the tubes from the rear headers and was highly heated and concentrated, the evolution of gas was rapid and the corrosion marked.

To rectify this condition, the water softener settling tank was fitted with heating coils and thus converted into a hot treatment system. Live steam coils were found necessary and the size of the softener was found to be such that the water would stay in it for about eight hours. Experiments showed that the complete break-up of the bicarbonate takes place in approximately five hours at 80° C. So when taken from the softener the water was practically free of soluble bicarbonate. The insoluble compounds were precipitated in the softener tank and blown out with the sludge. The high temperature of the water in the softener, due to the live steam treatment, boiled out the carbonic acid gas almost completely, but to eliminate the last traces of carbonic acid gas left in the water it was arranged to introduce the water into the hot well through a spray, which gave opportunity for the rest of the gas to escape. Of course this might introduce air into the water, but as between carbonic acid gas and air the air was held to be less injurious. Air was almost entirely absent from the hot well, which was enclosed and vented through a long pipe, and into which hot well steaming water returned from the coils at boiling temperature. The condensate from the turbine condenser, being brought back through a separate removal pump, was air free.

Immediately after the introduction of this hot water treatment the trouble with the boiler began to decrease, and in about three months had practically disappeared. In a period of one year afterward only one or two tubes broke down. Of course a few were bound to give out, as many tubes in the boiler had been pitted, and those which were almost gone would naturally give way when conditions were especially severe. However, the main trouble was entirely stopped. Incidentally the effectiveness of the softener for preventing scale was greatly increased.

The cost of installing this apparatus was very slight in comparison with the savings. The insulating covering of the heater,

including the necessary flues for gas discharge, etc., amounted to approximately $350. The high-pressure line and heating in the softener amounted to about $100 more. The heat losses of the softener were estimated at less than 1 H. P., and of course the heat used to raise the water to boiling was not lost, as it was practically all returned to the boiler.

DISCUSSION.

B. G. Worth: About this question of zinc, I think Mr. Speller did not mean he used zinc in its electrolytic relation. (In his de-activating system.) I think he meant it just to absorb the oxygen. Zinc used electrolytically acts in quite a different manner. Usually when zinc is put in boilers it does not work very well because it is put in in a poor manner; although Mr. Cumberland, whom Mr. Speller has just spoken of, shows in some of his propaganda how zinc that has been very well connected with the boiler also does not have the protective effect. Speaking of my own paper, our zinc was very well put into the boiler, connected with careful screw joints and tightly made connections, so the electrolytic currents or galvanic currents, whichever you want to call them, would travel very, very easily into the iron of the boiler, but this did not work—that is to say it did work in the drums of the boiler, but it did not work down in the tubes because the galvanic currents did not get down into the tubes. That is just one of the interesting points about that paper that I wanted to mention. Another point in my paper that particularly struck me is how you can sometimes use a hot softening system for softening water and get an additional effect that is not just a regular softening effect. I do not think you very often get the effect that we had at Keyport because the finding of carbonic acid gas in just that particular form is very rare. But it does show how a hot softening system can sometimes be used much better than a cold one.

F. N. Speller[1]: The scrap iron treatment referred to in my paper has no effect on the CO_2 contents, and we find practically no corrosion when the free oxygen is nearly eliminated, notwithstanding the fact that the carbonic acid is as high in leaving the

[1] Metallurgical Engineer, National Tube Co., Pittsburgh, Pa.

deactivator as it was before. There may be a very slight amount, that would not be noticeable in four or five years.

As to the Cumberland process, I have followed this with a good deal of interest. The Cumberland process consists of the use of positive electrodes by which they impose a current on the whole system, making the rest of the system electro-negative. The theory is fine and has apparently been worked out in practice in some types of boilers and condensers where all parts of the system are within a few feet of the positive electrode. I believe this system has been successful in marine condensers and in some cases in boilers. Of course, Mr. Cumberland, like a good many others, has no use for zinc plates attached to a boiler with the idea of making the boiler electro-negative, and I quite agree with him on this point. In the first place, the zinc plates are not usually firmly attached to the boiler so as to give an electrolytic connection, but you do get a chemical action from the zinc in removing the free oxygen, and that is, I believe, where the zinc has acquired its reputation for corrosion preventive in boilers rather than from the electrolytic protection which seems to be more or less uncertain in practice.

Colin G. Fink[2]: J. G. Taplay[3] communicated, in a detailed report, results of his investigation on the corrosion of dry gas meters. This report is being published in full by the Institution of Gas Engineers of England. On page 40 of this report, Mr. Taplay makes the following observations: "In the majority of chemical and electrolytic actions, water vapor must be present. Usually corrosion takes place at the dew point, that is, the temperature of saturation. Sometimes the water is necessary to dissolve the products of the chemical action as they are formed, otherwise the action ceases very quickly. Internal corrosion of gas meters may be brought about in at least six different ways as has been definitely shown. The first five processes are active in the presence of water vapor. In the case of the sixth, water vapor is not necessary. They are classified as follows, very much in the order of their destructive agency: (1) Hydrocyanic acid; (2) Products of Interaction of Carbon, CS_2 and NH_3; (3) Excess Oxygen; (4) Carbon Dioxide; (5) Sulfur Dioxide; (6) Dry Carbon Monoxide acting on Metallic Iron."

[2] Consulting Electrometallurgist, So. Yonkers, N. Y.
[3] Chemist, the Gas Light and Coke Co., London, E. C. 4, Eng.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

EXPERIMENTS ON THE CORROSION OF IRON AND STEEL.[1]

By T. S. Fuller.[2]

Abstract.

Records observations on the behavior of drops of water standing on pure iron and other metals; also standing partly on iron and partly on zinc or brass. Results of oxidation are usually perceptible in one minute and quite marked in 15 minutes. If the drop evaporates completely, well-marked zones remain on the metal. Progressive placing of fresh drops on the same spot, and allowing them to evaporate, showed that the first drop was much more active than subsequent drops, indicating that a partial immunity is progressively built up. Copper-steels were compared with cold-rolled wrought iron, showing copper to slow up the rate of rusting. [J. W. R.]

It has been the writer's privilege recently to observe certain phases of that most complicated and many sided phenomenon—the corrosion of iron, and he has endeavored in this paper to set forth the facts as shown by a few short experiments. The well-known assertion that iron containing a small amount of copper rusts much less readily than ordinary iron should cause those interested, particularly electrochemists, to take notice. There is nothing in their teaching which would have enabled them to predict this effect. The instinct to get at an understanding, while it may frequently seem to be merely a desire to support a preconceived notion, is probably in the final analysis a healthy step toward orderly advance in general. It is probable that when the manner by which copper benefits iron is understood a way may be paved for still further improving the quality of the metal.

[1] Manuscript received March 28, 1921.

[2] Research Laboratory, General Electric Co., Schenectady, N. Y.

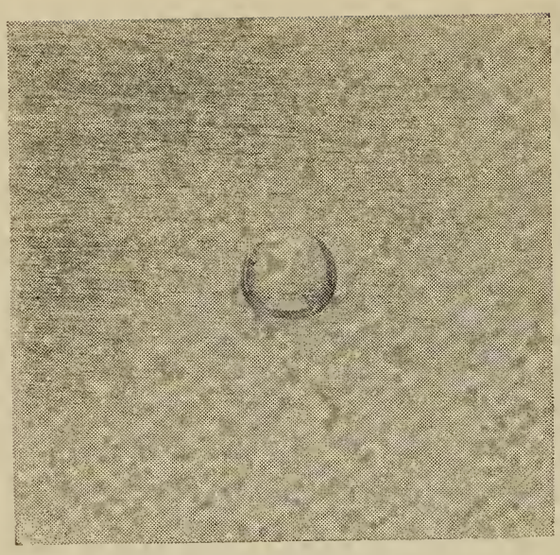


Fig. 1. 1 minute.

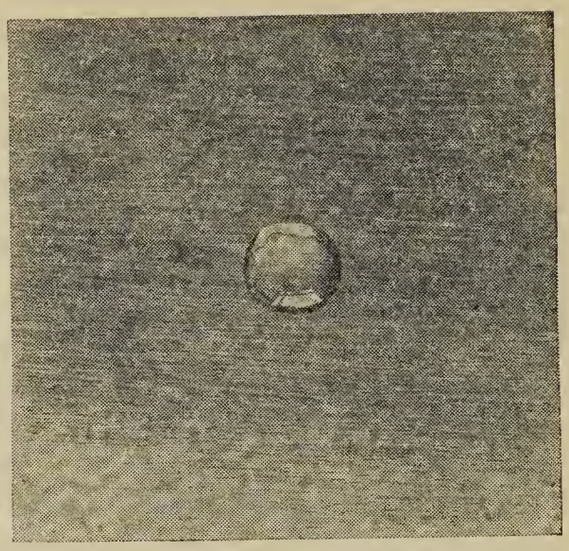


Fig. 2. 15 minutes.

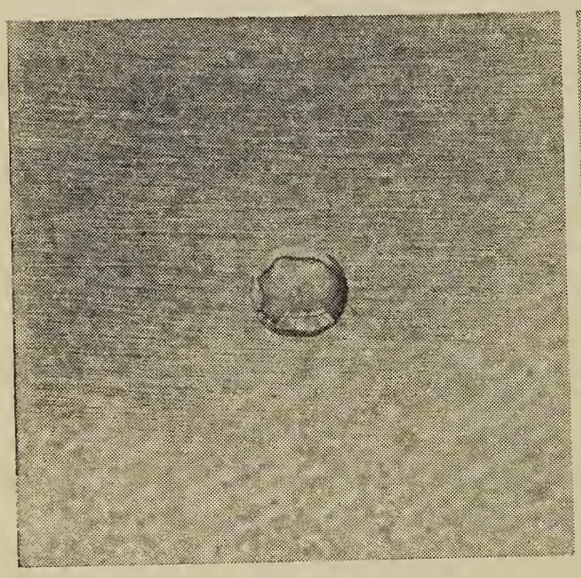


Fig. 3. 30 minutes.

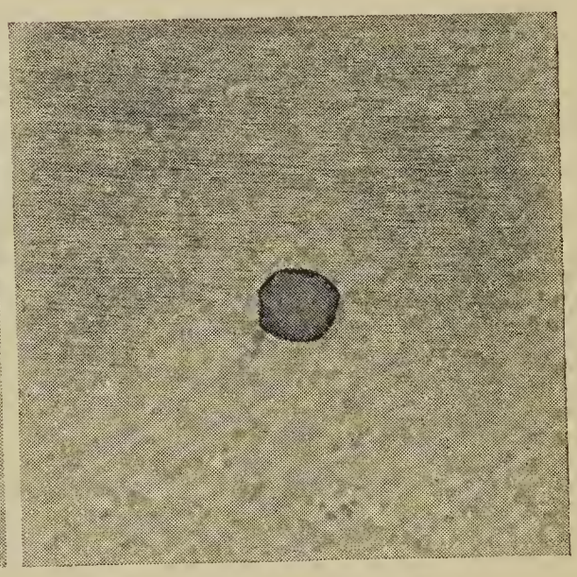


Fig. 4. 1 hour.

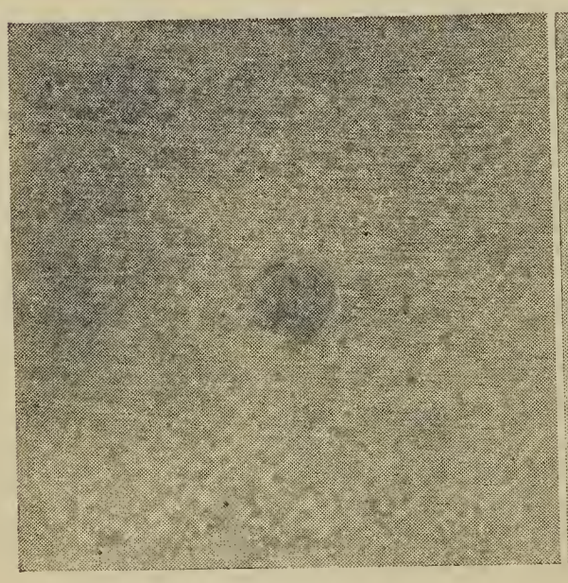


Fig. 5. Dry.

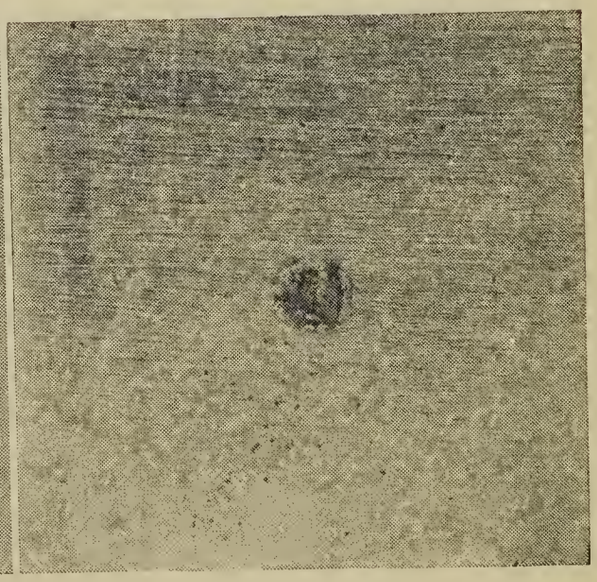


Fig. 6. Wiped.

Drop of Distilled Water on Cold Rolled Iron Surface.

It is furthermore probable that if a quick method of determining relative corrosion were available, more experimental work on iron alloys would be done. It is true that technology is mainly interested in the practical life of iron and not in academic questions, and yet it often happens that a more detailed understanding than the mere length of life is helpful in all forms of disease.

An iron roof or a wire fence does not corrode at a constant rate, and its life is so enormously affected by other factors, that it can not be said that it is known what is meant by rate of corrosion. Iron would never corrode if it were always dry. The moisture of the air can only bring about corrosion when it is deposited on the surface of the metal. A piece of cold rolled steel remains bright in steam at 100° C. even in the presence of oxygen, but whenever a drop of water condenses upon it, corrosion rapidly sets in.

Ordinary rusting as measured by the life of structures out of doors is a very complicated phenomenon. It certainly varies with the weather, is less when the metal is covered by a protective coating of paint or oil, is reduced by the presence of an adherent coating of rust, and particularly by the oxides of certain metals other than iron. The acid or alkaline characteristics of the air in the immediate vicinity are of the greatest importance as is the action of frost and freezing temperatures. Such factors must be met in practice, but they are not all present in many applications of iron and steel so that the out-door life test is far from an ideal one. It was thought that if a rough measure of the initial or the maximum rate of corrosion of iron could be found, it would very likely stimulate research on various iron alloys and serve to guide attempts to get rustless iron.

The method which has been used in these experiments is illustrated in Figs. 1 to 6. Samples of the metal were first washed in gasoline to remove grease, ground or filed until a bright, clean surface was insured and subsequently polished with clean, dry emery paper to leave a comparably clean, but not highly polished surface. A drop of distilled water which was in equilibrium with the air of the laboratory was then placed on the iron and watched through a lens. The final distribution of the product resulting from the corrosion of a drop of water on an iron surface at room temperature is characteristic in every instance, and may

be observed in Fig. 5. Three distinct zones are invariably present in every rust spot. An outer one showing light in the picture has been called by us the "immune" zone, an inner one which occupies a large part of the area of the spot, and a "wall" zone which lies between the outer and inner zones and shows as a dark line in the picture. The outer or "immune" zone is perhaps a half millimeter in width, and the "wall" zone is best described as a line.

At the end of two minutes after placing the drop on the iron a greenish-yellow ring is faintly visible on the part of the surface which later becomes the "wall" zone. At the end of four minutes this ring is very plainly visible and soon after a wall of hydrous oxide begins to develop and continues to pile up in this zone. Gradually the surface of the iron under the entire central portion of the drop turns green, then yellow-green, and finally as the water evaporates, yellow. The outer zone has during this time remained unattacked, or if attacked the products of corrosion have not been deposited within this zone, hence it has been called "immune." It appears that there may be a force either preventing corrosion at the edge of the drop, or else preventing the deposition of the rust at that point. In the case of areas of water larger than a single drop the immune zone is not so evenly defined, and, while occurring at the edges, it acts as though convection currents determined its development.

With the ordinary qualities of iron the first evidence of rusting under a drop of water in the air occurs at the same time. This need not have been expected, because it is possible that while the life of most ordinary irons and steels under identical rusting conditions is not very different, yet the rusting proper is retarded by so many influences that the maximum speed, or the initial corroding rate, might presumably vary greatly for slight differences in composition.

Figs. 1 to 6 illustrate the manner in which an iron surface is rusted by a drop of water and are self-explanatory. Fig. 1 was taken one minute after placing the drop on the surface of the cold rolled iron and shows no corrosion; Fig. 2 was taken 15 minutes after the start and clearly shows all three zones; Fig. 3, taken 30 minutes after the start, shows the three zones still better defined. The same applies to Fig. 4. Fig. 5 shows the result-

ing rust spot dry, but undisturbed, and Fig. 6 shows the same spot after the loose rust has been removed by wiping with a piece of filter paper.

It is perhaps fortunate for all of us that iron does not continue corroding at the rate at which it is attacked during its first few hours' exposure to water. A brief study of the progressive corrosion of iron has been made by applying successive drops of distilled water to the same spot of cold rolled iron. The drops covered a circular spot on the surface of the iron one-half inch in diameter. Each was allowed to evaporate in the air, and when dry the resulting rust was wiped from the spot by means of a piece of filter paper. Another drop of water was placed on the spot formerly occupied by the first, allowed to evaporate and its corrosion product wiped from the metal. This was done seven times and the amount of iron in the rust resulting from each drop determined.

Drop	Amount of Iron Milligrams
1	0.30
2	0.10
3	0.12
4	0.12
5	0.10
6	0.06
7	0.05

The iron in the rust produced by the first drop equalled nearly three times the amount produced by each of the four succeeding drops and five and six times that produced by the sixth and seventh drops, respectively. It appears that a partial immunity to corrosion is built up, by the corrosion product of the first drop, becoming progressively greater with succeeding drops.

If we consider the alloying elements and their effects on the immediate rusting of iron we might again easily lead ourselves astray by pre-conceived notions, and for that reason these simple experiments are worth careful trial. It is interesting to note the effects of plugs of brass, monel metal and zinc, riveted in cold rolled iron blocks, upon the distilled water corrosion of the iron, when the drop partially covers both the plug and the iron. Figs. 7 to 11 show the results of these experiments. Fig. 7 shows

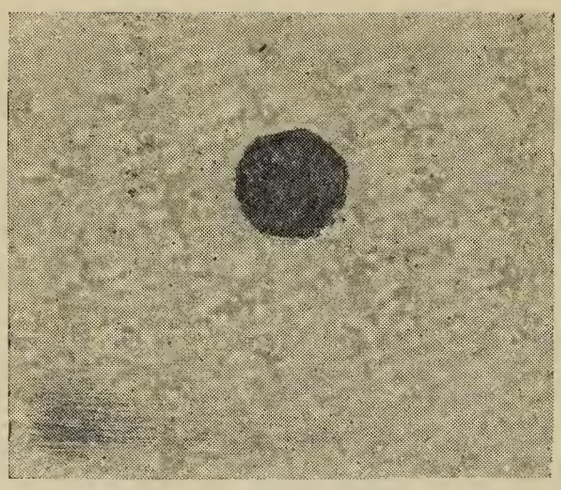


Fig. 7. Rust (dry) from drop of distilled water on cold-rolled iron surface.

Fig. 8. Rust (dry) from drop of distilled water covering parts of brass and cold-rolled iron surfaces.

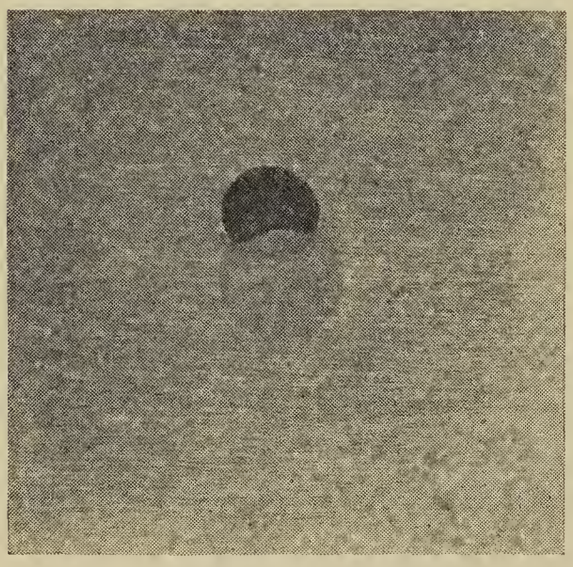


Fig. 9. Rust (dry) from drop of distilled water covering parts of monel and cold-rolled iron surfaces.

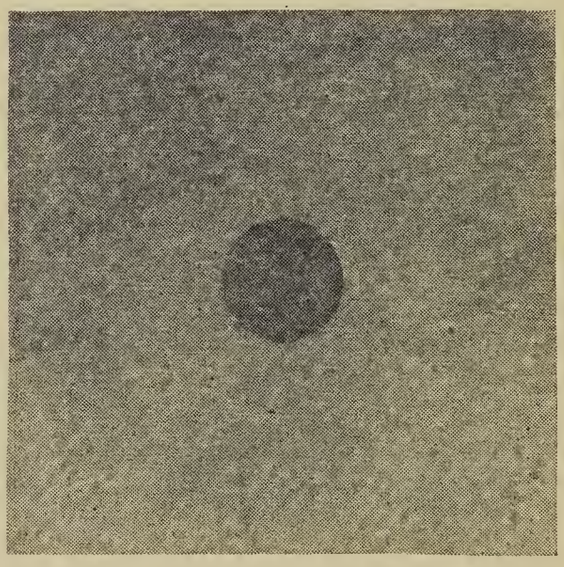


Fig. 10. Rust (dry) from drop of distilled water covering parts of zinc and cold-rolled iron surfaces.

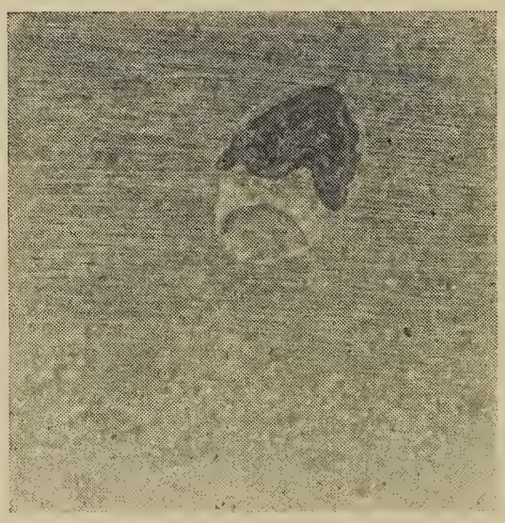


Fig. 11. Rust (dry) from large drop of distilled water covering parts of zinc and cold-rolled iron surfaces.

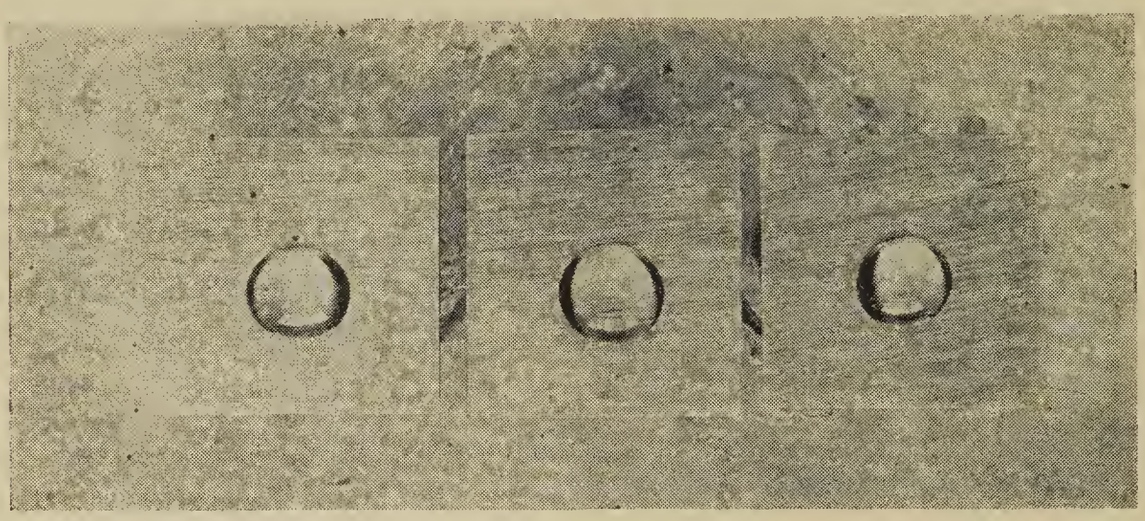
the rust resulting from a drop of distilled water upon cold rolled iron. Figs. 8 and 9 are very similar, the former showing the effect of a brass and the latter of a monel plug. The rust extends a little way over the edge of the non-ferrous plug in each case. Figs. 10 and 11 show the effect of zinc plugs. The zinc serves to inhibit entirely the corrosion of the iron within one-eighth to one-quarter of an inch (0.3-0.6 cm.) from the edge of the plug. Fig. 10 shows result of placing a drop of distilled water partially on the zinc and partially on the iron, but within the area of inhibition exerted by the zinc. In this case the only corrosion which has taken place is that of the zinc. Fig. 11 is similar to Fig. 10, except that a larger drop was used, extending well beyond the inhibition area exerted by the zinc and resulting in the corrosion of the iron outside the inhibition area.

Small amounts of aluminum in iron do not change the initial rate of corrosion judged by the visible effect of the first drop of water, but small amounts of chromium produce a marked effect. The presence of one percent of calcium does not alter the initial rate of corrosion of iron.

The tests performed in a manner already described have shown very interesting results when performed on certain copper-bearing steels. The difference in the initial rates of rusting between these and cold rolled iron, while easily detected at room temperature, is not great enough to allow sufficient time for photographs. The samples were therefore placed on ice, thereby retarding the corrosion rate to one-third or one-quarter of its value at room temperature, and magnifying the difference between the various steels. Two samples of copper-bearing steels were compared with cold rolled iron. The copper-bearing steels were sent to us by Mr. O. W. Storey, of the C. F. Burgess Laboratories, and showed the following analyses:

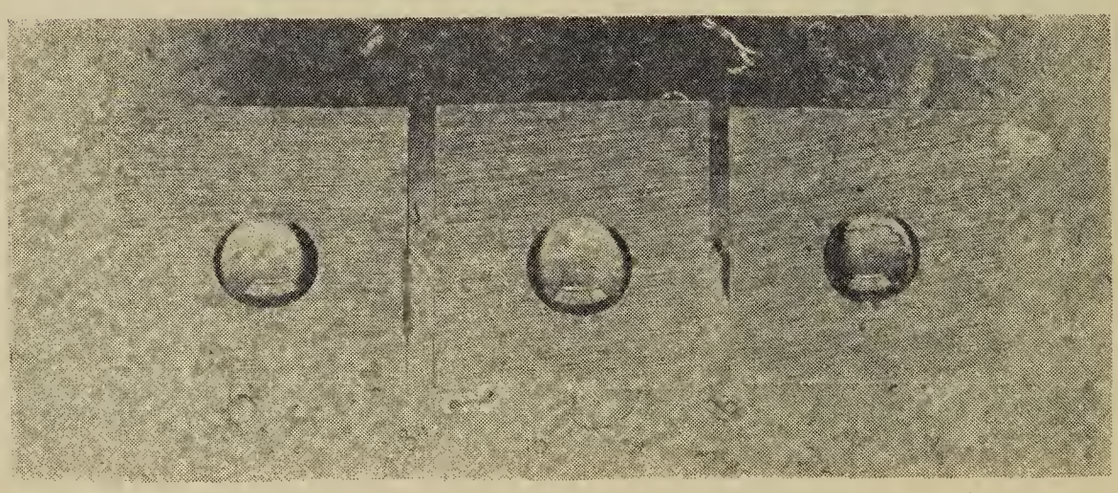
	C	Mn	S	P	Cu
Keystone.....	0.10	0.42	0.037	0.012	0.29
High-copper steel	0.07	0.44	0.026	0.012	2.57

Drops of Distilled Water on Surfaces of Cold Rolled Iron, Keystone Steel, and a High Copper Steel at Temperature of Melting Ice.



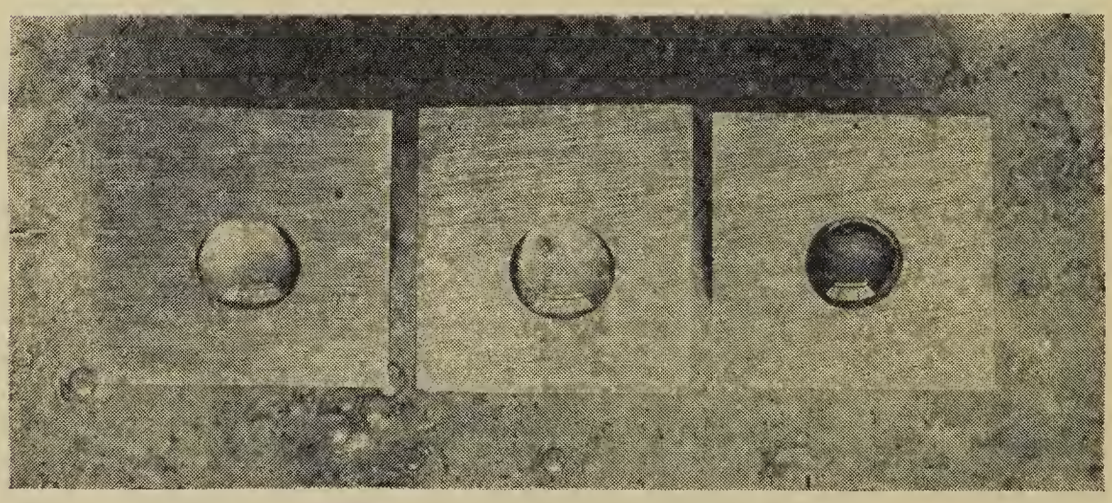
High Copper. Keystone. Cold Rolled.

Fig. 12. 1 minute. Ice.



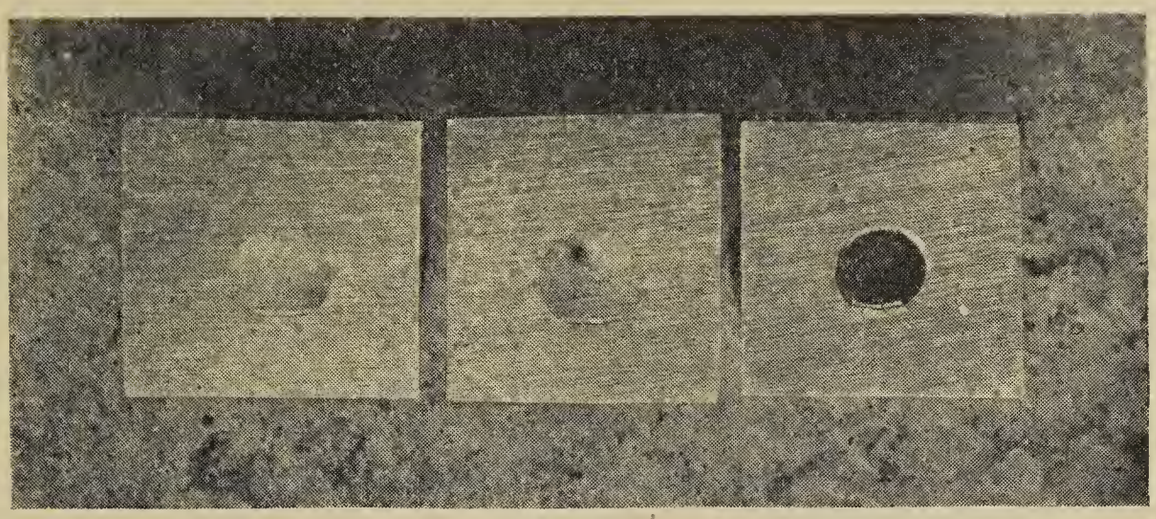
High Copper. Keystone. Cold Rolled.

Fig. 13. 1 hour. Ice.



High Copper. Keystone. Cold Rolled.

Fig. 14. 2½ hours. Ice.



High Copper. Keystone. Cold Rolled.

FIG. 15. 4½ hours. Ice.

High Copper. Keystone. Cold Rolled.

FIG. 16. Dry.

Figs. 12 to 16 show the result of these tests. Fig. 12 after one minute, Fig. 13 after one hour, Fig. 14 after 2½ hours, Fig. 15 after 4½ hours, and Fig. 16 after all the water had evaporated. Certainly this test shows a very great difference between the cold rolled sample and the copper-bearing steels. The rusting of the cold rolled steel has taken place quite normally except at a much reduced rate. The development of the three zones may be clearly followed in the series of pictures. Both copper-bearing samples show evidence of corrosion, the one containing 0.29 percent copper showing more than the one containing the larger amount of the alloying element.

It is not probable that copper is the only moderately inexpensive metal which when added in small quantities is capable of

slowing up the rate of rusting of iron, but it is quite probable that this generation or those to follow will discover an alloying element or group of elements superior to copper in this respect. The possible number of combinations of metallic elements which may be added to iron or steel in varying percentages is, of course, infinite, and it is reasonable to suppose that improvements in the art will proceed more rapidly if the investigators are able to conduct short experiments giving quick results than if each test extends over a period of years.

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DISCUSSION.

COLIN G. FINK[1]: In that one test in which you tried to demonstrate the gradual slowing up of the corrosion you say you did not remove the yellow rust, but you left it there.

T. S. FULLER: No, I did remove it.

COLIN G. FINK: If you had not, would not the presence of that rust increase the corrosion velocity?

T. S. FULLER: I think it would.

COLIN G. FINK: Instead of retarding it.

T. S. FULLER: I think what happens is this: If a drop of water be allowed to corrode an iron surface, apparently two distinct layers of corrosion products are formed—a red rust on top, and a layer of very adherent black material, probably a ferrous compound, between the red rust and the iron surface. I believe from our experiments that the red rust accelerates the corrosion and that the black corrosion product serves to inhibit it to a certain extent. The black product can not be removed by wiping with a piece of filter paper.

I would like to say that I have tried cold rolled iron annealed in hydrogen and annealed in air, with practically the same result that I have described in the paper.

[1] Consulting Electrometallurgist, So. Yonkers, N. Y.

W. D. RICHARDSON[2]: I wanted to add just a word in connection with the statements made by the last speaker with regard to these layers of rust. In a series of corrosion experiments which I made, beginning a number of years ago and reported in a paper last year before the American Institute of Chemical Engineers, I reported this black layer as prominently present in one series of experiments. Of course, the statement that the first product formed here is ferrous hydrate is correct. It could not be otherwise, but as the corrosion goes on there is formed a black magnetic layer which apparently is ferroso-ferric oxide, giving both ferrous and ferric salts when dissolved in acids. In this series I speak of, the layer was very tightly adherent, and apparently, on account of its adherence to the surface, it did protect it against further corrosion. I think it is simply its adherence that did it and not anything in principle in the substance itself, because it it is well known that such a magnetic oxide will form a scale.

J. A. AUPPERLE[3]: Having in mind stainless steel, containing out 12 percent chromium, the paragraph on page 205 by Mr. Fuller is not just clear. He says as follows, "Small amounts of * * * * ." I should like to know whether it increases the amount of corrosion or otherwise?

T. S. FULLER: Small amounts of chromium decrease the corrosion rate.

J. A. AUPPERLE: It inhibits corrosion?

T. S. FULLER: Yes.

COLIN G. FINK: Mr. Richardson brings up an interesting point, and that is as to the tenacity of that oxide film. Perhaps Mr. Buck can enlarge upon that. Is that not one of the reasons why copper steel does stand up.

D. M. BUCK[4]: That is my belief. As stated early in this discussion, the rust film formed on copper steel is an entirely different structure from the rust film on normal non-copper steel, and it has been my observation that it acts as a protector to the underlying metal. In figure 2 of my paper, if the curves were

[2] Chief Chemist and Chemical Engineer, Swift & Co., Chicago, Ill.
[3] Chief Chemist, the American Rolling Mill Co., Middletown, O.
[4] Metallurgical Engr., American Sheet & Tin Plate Co., Pittsburgh, Pa.

started at zero instead of at four months, a decided straightening out would be noticeable at four and eight months' exposure.

T. S. FULLER: I am convinced in my own mind that the black material does serve to slow up corrosion, not only from these, but from other experiments, which I described before this Society two or three years ago, in connection with the discussion of the penetration of iron by hydrogen. Hollow iron tubes, with iron plugs in one end, and glass U tubes having one end open to the air sealed to the other, were filled with mercury, and immersed in wet steam. The latter reacted with the iron, liberating hydrogen, part of which passed through the iron tube, displacing the mercury, and was collected in the closed and calibrated arm of the U. The penetration of hydrogen was very much more rapid where the surface of the tubes was bright, *e. g.,* when they were first immersed in the steam, than it was after the surface became coated with the characteristic black corrosion product resulting from the reaction between iron and wet steam.

In cases where the same sort of iron tubes were immersed in dilute acids, and where, of course, no black coating was formed, the hydrogen penetration became more and more rapid with time.

J. W. RICHARDS[5]: What Mr. Fuller says is in line with some old practice in the making of Russia iron sheets, that is, oxidized iron sheets. Some 40 or 50 years ago patents were taken out for putting a little bit of copper oxide on the surface of iron sheets which were being oxidized, for the purpose of giving the Russia iron finish, and statements were made that the oxide formed on the sheets in the presence of the copper was more elastic, that it would bend better, and it protected the iron underneath it better from rusting. The presence of copper in this black scale formed on the iron at the red heat gave to that scale rather physical properties of preventing corrosion, and made it more strong and elastic. It seems to agree with the modern experience that copper-iron oxide formed on copper bearing sheets is of a more continuous, tough or homogeneous character.

W. D. BANCROFT[8]: I would like to add to the occasion by bringing in the copper tin alloys. If you take a copper tin alloy

[5] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.
[6] Prof. of Physical Chem., Cornell University, Ithaca, N. Y.

and add more tin, the alloy becomes constantly more anodic—I am using that word so as to avoid any possible differences on the part of Dr. Richards—and consequently it should corrode more readily. As a matter of fact, the corrodibility passes through a minimum, because with certain of these copper tin alloys the tin corrodes to stannic oxide in such a form that it forms a coherent film over it and prevents further attack. The stannic oxide does not come down so as to form a protecting film. Further, I think we would get ahead a little more rapidly if everybody would make the distinction and speak about films protecting from corrosion, when they mean that, and not as against inhibiting corrosion. Take the case of the lead storage battery. We all know perfectly well that the presence of lead peroxide in contact with lead accelerates the corrosion of the lead, because that is what the action of the lead storage battery is. On the other hand, your peroxide electrode consists of lead coated with lead peroxide, and that does not corrode appreciably. Under those conditions you get a film of lead peroxide over the surface of the lead, which protects it. There we have the same two substances and the lead peroxide in one case acts as a protective coating and in the other case it acts as an accelerator of corrosion. I think the use of the word inhibit has been rather lax.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

A PRACTICAL ASPECT OF THE CORROSION PROBLEM.[1]

By John F. Thompson.[2]

Abstract.

Lays down the thesis that the use of any metal or alloy is rarely based upon the sole property of resistance to corrosion; that this, although always a necessary factor, is quite frequently not the determining one which governs practical serviceability. This is illustrated by considering various properties which are frequently the determining factors to which resistance to corrosion is secondary, such as hardness, resistance to abrasion and wear, strength at high temperature, tensile strength at low or high temperature, conductivity for heat or electricity, resilience, modulus of elasticity, absence of season cracking, color, avoidance of tarnish, non-sparking property, non-amalgamating.

[J. W. R.]

This symposium emphasizes a deep impression, long resident in my mind, of the basic importance of this source of economic loss to industry, and of the large expenditure of both scientific thought and practical effort which is yearly devoted to its mitigation. A most cursory glance through the scientific and technical literature will convince anyone of the extent of scientific interest in this subject, and the burden of solving in a practical manner the daily corrosion problems in industry actually constitutes the life-work of many of those present at this meeting. I am sure that they who carry part of this burden will readily agree that there is perhaps no other single problem which is of such frequent and troublesome occurrence in the operations and in the structures of industry of today.

[1] Manuscript received March 29, 1921.

[2] Manager, Technical Dept., The International Nickel Co.

If any generalized description can be given of our progress during the past fifty years in the field, it is perhaps this: that scientific thought seeking an intensification of our knowledge of corrosion and the establishment of an adequate theory, has been continually unsettled by our increasing practical experience which has steadily functioned to widen the scope of the problem, but not to deepen appreciably our fundamental knowledge of any portion of it. The now more or less classic corrosion theories—the carbon dioxide theory, the hydrogen peroxide theory, and the electrolyte theory, have never been able to satisfy entirely the needs of the art in its grapple with the problem, due to the increasing practical recognition of the profound influence on corrosion of other and apparently unrelated factors. Thus it was early demonstrated that there is a vast difference between corrosion in still and in flowing media, and it is known that the removal of the products of corrosion often exercises a great accelerating effect on its rate. More recently a large amount of very fine work by members of the British Institute of Metals has demonstrated the specific effect of the products of corrosion themselves on the corrosion rate, and has emphasized the effect of presence of foreign matter, condition, and mechanical and heat treatment of the material. Recently W. D. Richardson[3] has emphasized the effect of these and other variables, as well as that of the chemical nature of the corroding medium.

In a word, we recognize today that corrodibility is not a specific property, capable of exact definition, but may depend upon the greatest variety of incidental conditions. An excellent example of this fact is furnished by tinned copper roofing. A roof of this material on the Library of Congress in Washington (Bureau of Standards Technologic paper No. 90) became completely covered with pin holes in some areas, other areas remaining quite sound after eight years. Inquiry developed the fact that nails in the shoes of workmen and others walking in the gutters produced indentations from which the pin holes finally developed. Whether the sheets had been trodden or not determined wholly their resistance to corrosion.

Thus have we become less and less confident of our ability to theorize about the behavior of metals toward corrosion under

[3] Trans. Am. Electrochem. Soc. (1920), 38, 245.

actual service conditions, and the realization has grown that corrosion tests to be of practical value must be made in the field, or at least on a scale comparable with the science in question itself. The International Nickel Company conducts annually many simple corrosion tests of its materials, particularly monel metal, which, however, we are forced to regard merely as orienting tests, giving only rough indication of practical possibilities, and, although we know, for example, that in a laboratory test under carefully standardized conditions, rod monel will corrode in a 6° Bé. sulphuric acid (pickling acid) at 75° C. at an average rate of 0.0045 gram per square inch (7.2 g. per sq. m.) per day, we are undertaking a single program of tests on the corrosion of metals in pickling acid, to comprise over 3,000 single determinations.

We must admit that we are still on essentially empirical ground in our knowledge of "applied corrosion" and confess much reluctance in venturing far in a practical way except in the path of actual experience. In saying this I distinctly do not wish to be understood as belittling the contribution of theoretical and scientific investigation work on the specific question of corrosion, for I believe that through it alone can our ultimate understanding of the subject in its broadest aspects be satisfactorily completed. It is my desire, therefore, in this discussion, to display the reverse practical side of the corrosion picture, and present for your consideration certain of the practical aspects which are daily forced upon the attention of those of us who are engaged in the technology of non-corrodible metals.

The first and most important of these is that the use of any particular metal is rarely based upon the sole property of resistance to corrosion. In fact, I should like to venture the assertion that resistance to corrosion alone, although always a necessary factor, is quite frequently not the determining one of practical serviceability in any particular "anti-corrosion" piece of construction, but some other property often entirely unrelated to it. And as a corollary of this, I can state from my own experience that materials may be sufficiently resistant to corrosion for jobs requiring this property, but their actual use for it be quite out of the question on account of their failure in other and quite

distinct directions. As this is the principal thought which I should like to contribute to this symposium, I beg indulgence while I illustrate it with several examples coming within my personal experience with the nickel group of corrosion-resistance materials.

Hardness: This is a property which is rather generally desired, at least in corrosion-resistant materials of construction; it is often absolutely necessary. Thus monel metal would not have been adopted for the manufacture of gear systems for water meters or for table cutlery unless in addition to its resistance to corrosion, it had possessed the requisite hardness to enable it to function as a gear tooth and to take and retain a cutting edge.

Resistance to Abrasion and Wear: During the war the Navy Department sought a metal for its identification tags, upon which were to be etched the name and finger print of each seaman. Monel metal was in this case recommended by the Bureau of Standards because it was thought that not only would the fine lines of the finger print etching not be corroded away, but they would also not be worn away as would have been the case with a softer metal. In this case the white color of the metal, its high melting point and the ready possibility of uniform etching with nitric acid, were determining factors in the decision to use it for this purpose.

Resistance to Abrasion and Strength at High Temperature: Nickel castings have been used for some time by The International Nickel Company as rabble-shoes in their roasting furnaces. It is found that they retain their strength at the high temperatures used in roasting, they do not oxidize readily, or corrode in the sulphur atmosphere of the furnace, and, most important of all, they abrade to a very much less extent than cast iron, which they have superseded in this service.

Tensile Strength: One of the principal uses for monel metal is in the construction of pickling equipment for rolled steel, for which it is suited by reason of its resistance to the action of pickling acid, together with its mechanical strength, which is unaffected by the acids used. The same combination of properties makes this material of value in the manufacture of fly screens; the superior strength of the material makes it possible to secure

adequate strength in the screen with finer wire and consequently with greater transverse visibility.

Resistance to Oxidation and Retention of Strength at High Temperatures: One of the recent developments in the utilization of monel metal has been its use in the manufacture of gas-engine exhaust-valves, both for automobile and airplane engines. Such a valve is called upon to retain its contour and surface sufficiently to effect a gas-tight seat at all times, and at the same time must be strong enough to withstand the mechanical strain on the shoulder of the valve. A similar case illustrating the value of this combination of properties is the use of a manganese-nickel alloy in ignition points in gas engines.

Electrical Resistivity: Electrical heaters in street cars are made both of monel metal and of constantan, the value of these materials for this purpose being due to their high electrical resistivity, together with their freedom from corrosion, particularly during such times as the cars are not in use. A material such as high-nickel steel, which also has a satisfactory electrical resistivity, is liable to rusting during such inactive periods. The same combination of properties has caused the selection of monel metal as a heater in the sterilization of dental instruments, in which water is dropped upon the red-hot heating element.

Thermal Conductivity: Monel metal is used in the doors for electric ranges partly because it does not rust, and partly because it increases the thermal efficiency of the range, on account of its low heat conductivity.

Resilience: This property, coupled with non-corrodibility, is demanded in valves in certain air compressors, where steel has not been suitable on account of rusting and where brass and bronze have also failed through corrosion.

Modulus of Elasticity: The efficiency of marine propellers being largely influenced by the size of the cross sections of the blades, this property has been studied to aid in the selection of a material which would resist distortion at the working pressure. It is necessary that this property be combined with those of resistance to corrosion and erosion.

Season or Corrosion Cracking: A number of metals and alloys, particularly certain compositions of brass, are subject to this peculiar type of failure, by reason of which they have often been adjudged unreliable for certain classes of service, although in point of resistance to corrosion alone they are not to be classed as inferior materials. It is found that copper-nickel alloys and monel metal are not subject to corrosion cracking, and these materials have been substituted satisfactorily in many cases for brass to avoid danger from this type of cracking.

Color: It is not usual in this day and age to attempt the imitation of cheapness in appearance, but, strangely enough, monel metal has actually been used in one or two cases, namely as bolts and padlocks for manhole covers in the New York streets and for identification nails on railroad ties, by reason of the fact that it is resistant to corrosion and looking exactly like steel, is therefore not subject to the predatory efforts of those who are in the habit of carrying away similar articles made of copper and brass. Similarly, monel metal and nickel have been used for eye-glass rims, supplanting gold and copper-colored articles for this purpose by reason of the elimination of yellow glare and reflections thereby effected.

Avoiding Discoloration: In many cases not only is resistance to corrosion required, but it is also necessary that the products of such slight corrosion as does actually occur shall not discolor or affect undesirably the material with which it is in contact. Thus monel metal has been used in the construction of kettles for boiling varnish, because it is possible to obtain in such kettles a whiter and more nearly colorless varnish than by the use of iron or copper. Similarly, monel is used in the form of screen for the drying of gelatine and glue, which it is claimed are not discolored by contact with it as much as by contact with copper, brass or bronze.

Not Pyrophoric: Monel metal is used in the construction of powder filling machinery because of its resistance to corrosion, and the very necessary property that it is not possible to produce a spark by striking it.

Amalgamation: Monel has been found to be very suitable for the construction of mercury gauges, supplanting copper and brass for this purpose, because of the fact that it does not amalgamate with the mercury, and is supplanting steel for this purpose by reason of the fact that it does not corrode.

Perhaps these few examples will have emphasized the truth of my thesis, of which possibly the first moral is that for any particular service a group of properties is always sought of which resistance to corrosion is necessary but not always determinative. It is in this form that the problem always presents itself to the engineer, and for the solution of which he reviews the status and suitability of present-day materials.

Present-day materials are what might be called specialized materials—specialized generally not only in good but in bad qualities. One has only to think of lead-coated materials, chemical stoneware, and the silicon-irons, to realize that most of them, although well qualified in resistance to corrosion, are seriously burdened with deficiencies in other directions. And if not, their merits and demerits must be weighed and ultimately distinct disadvantages may have to be tolerated for the sake of the corrosion-resisting quality, which in many cases forces a radical change of design. If, therefore, any conclusion may properly be drawn from these observations, we might, in sympathy for the unfortunate situation of the engineer, draw this one: that he is greatly in need of a material of corrosion-resisting properties which, in addition, is otherwise well-balanced in its physical characteristics and without serious deficiencies. Generally speaking, it must be reasonably hard and resistant to abrasion; it must be refractory to heat. Above all, it must be readily subject to the usual processes of fabrication: welding, soldering, forging, casting, machining, rolling, drawing, stamping, etc. It is in this respect that most of the specialized corrosion-resistant materials display marked inability to meet the requirements of the situation fully without expensive and troublesome changes of design.

Finally, a material to be generally useful must be available in commercial forms. The importance of this qualification will be fully appreciated by all of those who have been familiar with commercial development of any sort, and who have realized how

vast is generally the step measured in time, energy and money between the laboratory report and the commercial *fait accompli.* It does not, however, seem to be recognized as generally as it should be that the effort requisite in developing a material to the point of commercial production has also of necessity created a fund of vital information about the material, often not possible of expression in mathematical terms, but generally of the utmost practical value.

How many enthusiastic inventors of new alloys (as well as of other improvements) have we not had to impress with the fact that a hard road of development lying before them must be traversed before they can have acquired the practical experiences in the manufacture and fabrication of the alloys necessary to their real and substantial exploitation for any purpose. In other words, we may profitably add to our category of useful characteristics of materials, not only to resist corrosion, but for all purposes, what might be called its "experience factor;" *i. e.,* the extent of our accurate practical and theoretical knowledge concerning it, and I think we can all agree that the value of this can hardly be overestimated.

DISCUSSION.

J. W. RICHARDS[1]: I want to call attention to two very important points. In editing this paper, I transposed the grams per square inch of corrosion per day into grams per square meter per day. It seems to me that that forms a pretty good number in which to place it. It becomes, for instance, 7.2 grams per square meter per day instead of 0.005 grams per square inch. I think putting it in the metric system in those units is a very convenient method of measuring corrosion. On page 217, Dr. Thompson says: "Monel metal is used in the doors for electric ranges partly because it does not rust and partly because it increases the thermal efficiency of the range, on account of its low heat conductivity." It strikes me that it is not the low heat con-

[1] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

ductivity at all, because almost all the metals have high heat conductivity, but its low heat emissivity or radiating power must be its useful property in this respect.

COLIN G. FINK[2]: I should like to amend Dr. Richards' suggestion in changing that standard to grams per square centimeter per year, because what most of the corrosion people are interested in is that y e a r , and that is what you want to impress upon the public; d a y is not a good advertising term.

J. F. THOMPSON[3]: I am not entirely in agreement with Dr. Richards on that point. The heat conductivity is exceptionally low and troubles us in a great many cases. The heat conductivity is perhaps one-fifteenth that of copper; that of some of the chromium-nickel alloys is even lower. It is one of those balancing properties which in some cases help us and in other cases hurt us, and I think its low heat conductivity i s the reason for monel's use in ranges rather than its emissivity properties.

COLIN G. FINK: It is on account of a combination of the two properties.

J. F. THOMPSON: Probably.

[2] Consulting Electrometallurgist, So. Yonkers, N. Y.
[3] Manager Tech. Dept., International Nickel Co., New York City.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

METAL PROTECTIVE PAINTS.[1]

By Henry A. Gardner.[2]

Abstract.

A chemical classification of the substances used as paints on metallic structures. The discussion indicates which are best to come in direct contact with the metal, which are best used for upper coats, insulated from the metal, and the desirable properties of the finishing surface paints. [J. W. R.]

The causes underlying the corrosion of steel, and the principles to be adopted in designing protective paints are well understood as the result of comparatively recent work.[3] In fact, the manufacture of the majority of high-grade paints now produced is based upon these principles. Briefly stated, they are as follows:

1. Basic substances in sufficient concentration inhibit the corrosion of iron. Basic pigments that are effective for this purpose are litharge, red lead, blue lead (basic lead sulphate), white lead, zinc oxide.

2. Chromic compounds (soluble bichromates), even in great dilution, prevent the corrosion of iron. Chromate pigments that are similarly effective when used in sufficient amounts are as follows: basic lead chromate, normal lead chromate, zinc chromate.

3. Neutral substances that do not ionize to acid reaction are considered inert. So-called neutral or inert pigments, such as iron oxide, which do not excite corrosion, produce with linseed oil very durable films. Such pigments include black, brown and red oxides of iron, china clay, silica, talc, and barium sulphate.

[1] Manuscript received January 26, 1921.

[2] H. A. Gardner Laboratory, Washington, D. C.

[3] Corrosion and Preservation of Iron and Steel—Cushman and Gardner; Paint Researches—Gardner; Papers on Paint and Varnish—Gardner.

4. Substances that form a galvanic couple with steel in the presence of moisture cause rapid corrosion. Pigments which act in this fashion (graphite, carbon black, lampblack) are used only as constituents of the finishing coats on steel surfaces, when first insulated from the metal by a coat of basic or chromate pigment paint. These carbon pigments with linseed oil form very durable and water-resisting coatings.

From the above data it is apparent that paints for priming steel should preferably be made of a substantial amount of one or more basic or chromate pigments, and that these paints should be covered with water-resisting finishing coats of carbon or iron oxide paints. For instance, steel that has been primed with high-grade red-lead paint and finished with two coats of a carbon paint will be protected from corrosion under most conditions for a long period of time.

In many instances, high-grade proprietary primer paints contain a mixture of red lead, chromate pigments, iron oxide and zinc oxide. The finishing coats of such paints contain carbon black or lampblack, generally with 5 percent of litharge, and often certain amounts of iron oxide and silica. The liquid for such paints is raw or boiled linseed oil with a total of about 15 percent of liquid drier, turpentine or mineral spirits. Where high gloss is desired, the addition of spar varnish is indicated.

In many places the use of black or other dark colored finishing paints may be objectionable from an esthetic standpoint or because of their gloomy appearance. Light-gray paint made of white lead and zinc oxide, or of zinc oxide and barium sulphate (navy practice), tinted with lampblack, have been used as finishing coats on steel bridges, government structures and vessels. While possibly not as durable as red or black paints, they give much higher light reflecting values and are of more pleasing appearance. For use around acid and chlorine factories, black bituminous coatings have usually been adopted. Of recent years, however, there has come a demand for white and light-colored paints. The only white opaque pigment for such paints that is insoluble in most acid gases is titanium oxide. This pigment, which is now produced by an electrochemical process and contains 25 percent of titanium oxide precipitated on 75 percent of barium sulphate, possesses tremendous hiding power. It is usually applied with up to 40

percent of zinc oxide to give it sufficient hardness. In white or tints, such mixtures are very durable.

Various metal powders are now being applied to some extent as constituents of metal protective paints. When applied direct to steel surfaces, zinc powder and aluminum powder have much greater rust-preventing properties than the powders of other metals, on account of the high electro-positive nature of zinc and aluminum. Because of the great light reflecting properties of aluminum powder, its use is indicated for special purposes on exterior work. Probably the most satisfactory liquid for suspending this powder is a high-grade exterior spar varnish. When used with linseed oil, a rather slow drying paint results.

CONCLUSION.

Standard painting practice for iron and steel calls for the application of a primer containing basic or chromate pigments. Finishing coats generally contain red oxide or black carbon pigments. A wider use of white and light-tinted paints of high light reflecting power is indicated for many purposes as finishing coats.

DISCUSSION.

P. R. Farrow[1] (*Communicated*): This paper is of intense practical value to the engineer interested in the protection of steel structures from corrosion and should awake interest and provoke discussion. The general statements made are of value, but do not go far enough to be of substantial value to those interested. My own experience with the protection of the interior of steel penstocks with water containing a relatively large amount of oxygen and subject to algae and diatom deposits and spongillae growths is a case in point. The experience here would show that pure red lead as a first coat carefully applied to the surface after thorough cleansing, followed by a coat or coats of mixed red lead and graphite gave very good protection. An empirical rule in old textbooks stated that red lead used for a primer must be "pure" and,

[1] Resident Engineer, Kaministiquia Power Co., Ltd., Kakabeka Falls, Ont.

as this point is borne out by experience, the common impurities which one would think would also be basic apparently have a somewhat deleterious effect upon the original coat. This seems to be admitted in the words "steel that has been primed with high-grade red lead paint" . . . *et seq.* in the paper, and it would be of interest to know what deleterious substances might be found.

Considering the above statements and those contained in the paper, which one would think would be common knowledge with paint companies' experts, it is curious to find them urging the use, apparently in good faith, of either coal tar products, straight graphite paint or mixtures of red lead and graphite for primers, in steel work exposed to extreme corrosive conditions. There is evidently need for educational work along the lines of the paper.

One other point: If soluble bichromate compounds prevent corrosion of iron, is it to be understood that a solution of such substances as potassium bichromate in water, applied to an iron surface before the application of a primer, might be expected to have a marked beneficial effect, or merely that the addition of a solution of chromic salts (in what solvent?) to the paint would have the desired effect? Or is it merely to be understood that the incorporation of chromic salts with the paint pigment is the desideratum?

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

SOME TYPES OF NON-FERROUS CORROSION.[1]

By H. S. Rawdon.[2]

Abstract.

Although fundamentally similar, the author discusses structural changes caused by corrosion of non-ferrous metals as four distinct types, namely (a) Selective attack of certain constituents, (b) Intercrystalline brittleness, (c) Internal oxidation, (d) Simultaneous action of stress and corrosion. As examples of each type the following are given: (Type a)—Brass (60 percent Cu 40 percent Zn) was exposed to sea water for 7 years. The α constituent (65 percent Cu) was untouched, while the β constituent (50 percent. Cu) was corroded by a leaching out of the Zn. (Type b)—Cable sheath of Pb exposed underground became brittle due to the destruction of the intercrystalline material (usually non-miscible impurities such as Fe, Cu, Ni, Zn, or miscible eutectic-forming elements as Sn or Sb). This type of corrosion can be induced by immersion in lead-acetate solution. (Type c)—Boiler safety plugs of Sn deteriorated by change of metal to infusible oxide under influence of moist heat. The same type of change is found with Al-Zn (15 per cent.) alloys. In this case moist heat causes the oxidation and swelling of the eutectic matrix. (Type d)—Brass and lead under combined stress and corrosion will fail far below normal stress. This is due to selective corrosion of the β constituent in the former, and to intercrystalline brittleness in the latter. [C. H. E.]

I. INTRODUCTION.

In the corrosion of metals and alloys, that is, the gradual oxidation by which the material reverts to the stable or oxidized

[1] Manuscript received February 12, 1921.

[2] Physicist, Bureau of Standards, Washington, D. C.

form, many interesting structural changes often occur. A study of such changes in the structure of the metal throws considerable light upon the general subject of corrosion and particularly upon the various contributing factors by which the process is accelerated. The non-ferrous metals and alloys, because of their great number and variety, afford more striking illustrations than does the class of ferrous alloys, although the corrosion of the latter class of materials is usually considered of much more importance.

The discussion of the various examples listed below as types is not intended in any way as a complete summary of this phase of the subject of corrosion. The cases cited are some which have come to the author's attention and are given to illustrate some of the principles which should be borne in mind in the study of corrosion in any form.

II. STRUCTURAL CHANGES CAUSED BY CORROSION.

1. *Selective Attack of Certain Constituents.*

The type of corrosive attack which may result in alloys which have a duplex structure, that is, alloys consisting of more than one kind of metallographic constituent, is well shown by brass of the type of Muntz metal. A typical composition for such material is essentially 60 percent copper and 40 percent zinc; the alloy has a structure similar to that shown in Fig. 1b. The two microscopic constituents which make up the material differ considerably in composition, both with respect to each other and also with reference to the average composition of the alloy as a whole. The α constituent contains approximately 65 percent and the β, 52 percent of copper. Figs. 1 and 2 show the condition which may result from the corrosion of such alloys in sea water. A weak, brittle substance, a *fac-simile* of the original piece in shape and size, remains after the corrosive attack which consists essentially of an electrolytic "leaching out" of the zinc from the material. The difference in the electrochemical properties of the two constituents, the α and the β, is fundamentally responsible for the form the corrosive attack assumes, though other factors also influence the rate of deterioration.[3]

[3] H. S. Rawdon, Typical Cases of The Deterioration of Muntz Metal (60: 40 Brass) by Selective Corrosion. Bur. Standards Tech. Paper No. 103. 1917.

The zinc is readily leached out of the zinc-rich, β, constituent, leaving behind a weak, pulverulent substance filling the spaces within the α matrix and thus rendering the whole alloy weak and brittle. The name "de-zincification" has been used to describe the process. Much of the zinc lost by the alloy exists as incrustations of basic or oxy-zinc chloride on the surface or embedded within the porous material. The α constituent may remain quite immune from attack for a long period, as is shown in Fig. 1c, which represents metal exposed for seven years in sea water. In other cases the attack of the α matrix follows soon after that of the β constituent, as was the case in the material shown in Fig. 2. The initial condition of the alloy, with respect to the annealing it has received, appears to determine this to a large extent. The material shown in Fig. 1c was thoroughly annealed before use, as is shown by the presence of numerous twinned layers within the α crystals.

It may be noted in passing, that the addition of small amounts of tin, approximately 1 or 2 percent, is sufficient to inhibit deterioration of metal of this kind in sea water.

2. *Intercrystalline Brittleness.*

A rather striking type of deterioration which may result from corrosion, manifests itself as an embrittlement of the metal. Lead is a typical example of this and it has also been reported in aluminum. After a very severe attack the metal becomes so brittle that it can readily be crumbled into powder, though it can be readily shown that each particle or grain still retains all the intrinsic properties of the parent metal. In the case of lead, which has become embrittled in this way, each detached grain is malleable and has all the other characteristics of lead but the "bond," between the individual grains or crystals, has been destroyed. Fig. 3 shows a specimen of lead which developed intercrystalline brittleness by corrosion during service as a cable sheath in an underground conduit.

This type of deterioration can be readily induced in lead by a simple immersion in a mild corroding reagent, for example, an aqueous solution of lead acetate. If a trace of acid is present, however, the attack is much more vigorous. Fig. 3 shows the change produced in lead treated in such a manner. The rate

of the attack is determined largely by the purity of the lead; metal of commercial grade, which of course always contains an appreciable percentage of impurities, is much more readily attacked than very pure metal. It has been shown, however,[4] that an appreciable embrittlement may be produced in lead of exceptionally high purity (99.993 percent) by immersion in normal lead acetate solution for a period of 24 days.

The following is the composition of a specimen of commercial lead chosen at random: Antimony, 0.07 percent; iron, 0.02 percent; tin, 0.14 percent; copper, nickel and zinc, not detected; lead (by difference), 99.72 percent. Practically all the impurities which occur in lead are insoluble in the metal, even in the molten state, hence they will exist in the solid metal as lodgements between the grains. Also such elements as tin and antimony, which are miscible in lead in the molten state, will exist in the solidified metal between the grains,—in this case as a eutectic film. The preferential attack of these intercrystalline constituents and impurities will account, then, for the intercrystalline embrittlement which is brought about by a corrosive attack of the metal. That such an attack is truly intercrystalline is plainly revealed by Fig. 3.

3. *Internal Oxidation.*

A type of internal corrosion by which a metal is gradually converted into a solid mass of oxide is illustrated by Fig. 4. Safety boiler plugs of the fusible type consist of a casing usually of bronze, with a filling of pure tin. Serious accidents have resulted from the deterioration of such plugs by the gradual conversion of the tin filling into a hard, infusible mass of stannic oxide. The oxidation, or corrosion, of the tin has been shown[5] to be accelerated by the presence of small percentages of contaminating metals, notably zinc.

Figs. 4a and 4b show the appearance of a plug in which corrosion had proceeded to such a stage, that practically all the tin had been converted into oxide. The failure of this particular plug to function properly was responsible for a very serious accident

[4] H. S. Rawdon, Intercrystalline Brittleness of Lead, Bureau of Standards Sci. Paper No. 377.

[5] G. K. Burgess and P. D. Merica, An Investigation of Fusible Tin Boiler Plugs. Bureau of Standards Tech. Paper No. 53.

with loss of several lives. Fig. 4c shows how the internal oxidation spreads throughout the tin as a branching tree-like network. Apparently the eutectic of zinc and tin which exists as an intercrystalline film is the portion most readily oxidized under the influence of heat and moisture. This gives rise to the internal network which gradually widens and thickens as the adjacent crystals of tin are corroded until practically the entire filling becomes oxidized.

The deterioration of certain zinc-aluminum alloys is a case of a similar type of internal oxidation. Certain aluminum alloys of high zinc content are sometimes used for small cast parts, often for die castings. The one shown in Fig. 5 was a fuse-box cover; after several years' use in a tropical climate it became warped and buckled as shown, and the surface was covered with characteristic "alligator" cracks. The alloy also hardened very appreciably during this time. The material which was of the composition: aluminum, 15 percent; lead, 0.4; zinc remainder, has a structure very similar to that shown in Fig. 5e, that is, a skeleton of a compound of aluminum and zinc, Al_2Zn_3, with a eutectic matrix. Fig. 5d shows how alloys of this composition behave when exposed to the combined effect of heat and moisture. The alloy swells and cracks under such conditions, although heat alone, at the same temperature (Fig. 5c), has no appreciable effect.

The mechanism of corrosion is essentially the same as in the tin filling of fusible plugs. The eutectic is readily oxidized under the combined action of moisture and heat, and this gives rise to the swelling of the piece and cracking of the surface. The cracks also penetrate into the interior as shown in Fig. 5e, and for the most part lie in the eutectic matrix.

4. *Simultaneous Action of Stress and Corrosion.*

The application of stress, particularly tensile stress, to a metal which is being corroded, often causes the failure of the part, although the applied stress may be considerably below that considered as a safe working load under ordinary conditions.[6] Fig. 6

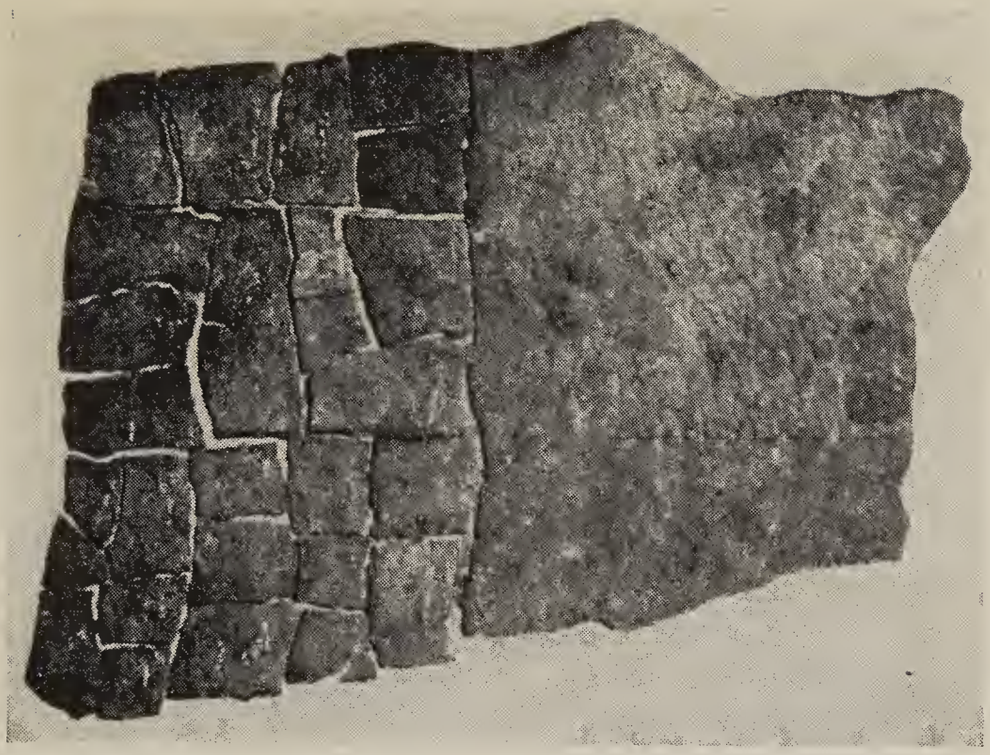
[6] P. D. Merica, Effect of Corrosion on the Ductility and Strength of Brass. Bur. Standards Tech. Paper No. 83.
Also P. D. Merica and R. W. Woodward, The Behavior of Wrought Manganese Bronze Exposed to Corrosion while under Tensile Stress. Bur. Standards Tech. Paper No. 135.

illustrates a case of corrosion of α-β brass under such conditions. The head of a Muntz metal bolt dropped off "of its own accord" in service. Fig. 6a shows the appearance of the fractured face of the head, x'-x', being the diameter of the shank of the bolt. The examination of the microstructure in the smooth portion of the fracture x'--x and x---x' at the extreme edge of the break as seen in a longitudinal section showed that a selective attack of the zinc-rich or β constituent (See Type 1) had resulted, Fig. 6c; while in the rough central portion of the break no evidence of corrosion appeared.

It can be readily shown that corrosion of such alloys at the apex of a narrow groove is much more intense than elsewhere in the same sample if the specimen is subjected to a tensile stress while surrounded by the corroding agent, as for example in this case, sea water. Fig. 7 illustrates local corrosion induced at the apex of a very narrow circular V-notch in a cylindrical specimen of Muntz metal stressed in tension while surrounded by a solution of salt (sodium chloride). The stress is not uniformly distributed across the section of the specimen at the notch, the unit stress at the apex of the groove being much higher than the unit stress elsewhere in the same cross section. This accelerated the corrosion along the apex of the narrow V-notch.

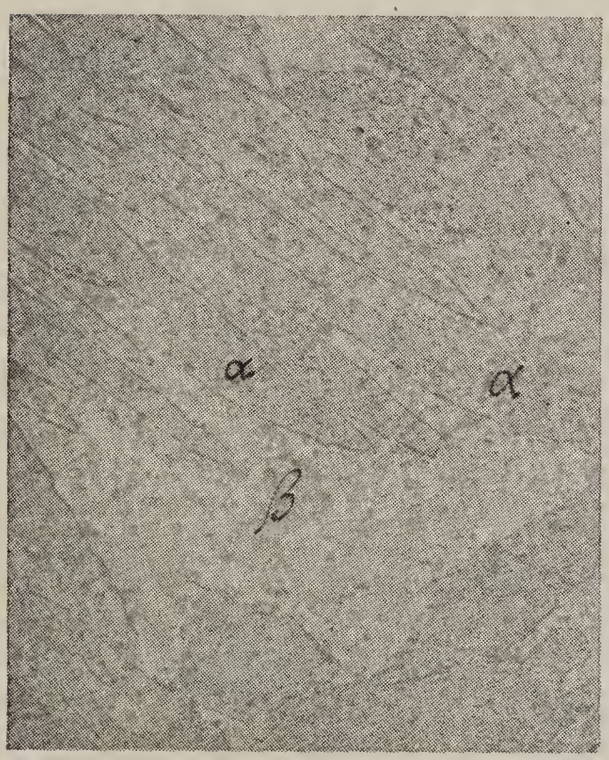
This aids in the explanation of the failure of the bolt head, Fig. 6. Under the combined action of corrosion due to sea water and the service tensile stress carried by the bolt, the portion of fracture x'--x, was gradually produced; this resulted in a fracture having the appearance of a "detail" or fatigue break. When the cross-sectional area became small enough so as to break under the applied loading, the central portion broke as a simple tensional fracture. The microstructure confirms this; the β constituent in the portion x'-x, shows evidence of deterioration by dezincification while in the central portion the alloy has remained sound and unchanged up to the extreme edge of the fracture.

Other metals often behave similarly. Fig. 8a shows the surface appearance of a rod of lead (99.99 percent) which was corroded while stressed in tension, the applied loading being equal to one-quarter the breaking strength of the material, 1790 lb./in.^{2}, as determined in the ordinary manner by the tension test. The



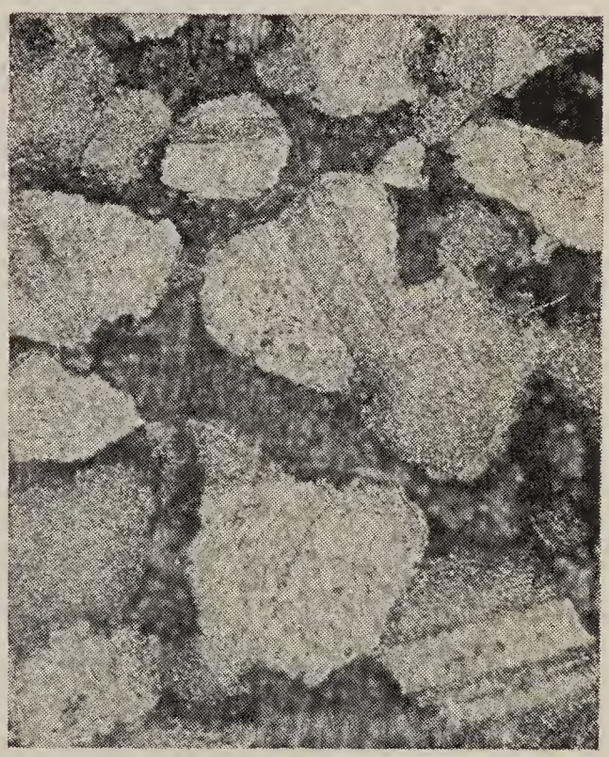
x 1

a. The brass sheet, approximate composition; copper 60; zinc 40 percent, became so brittle after corrosion in sea water that it could be broken into fragments, as shown, by the fingers alone.



x 500

b. Micro-structure of a Muntz metal sheet showing the two constituents, α and β. Etching reagent, ammonium hydroxide and hydrogen peroxide.



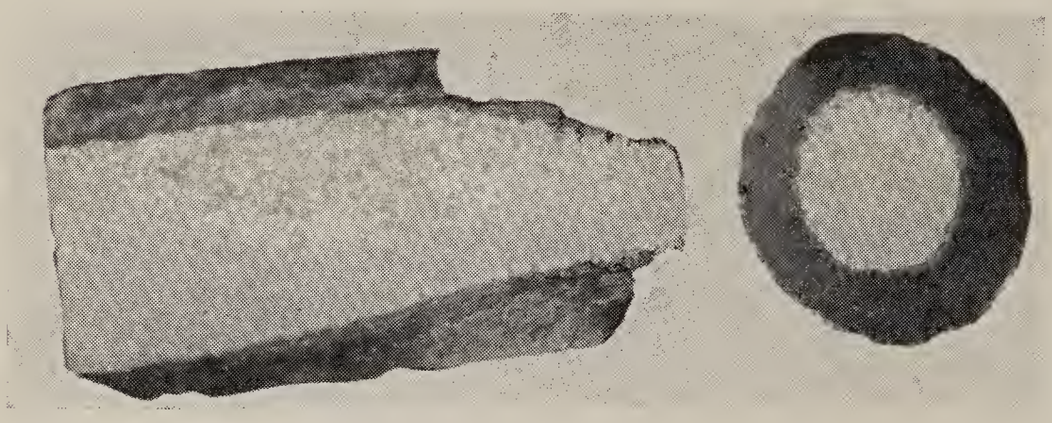
x 500

c. Micro-structure of corroded sheet of Muntz metal, "a" above, after 7 years' exposure in sea water; the β constituent has disintegrated into a weak pulverulent material resembling copper. Etched with ammonium hydroxide and oxidized in the air.

FIG. 1. Appearance of a corroded brass sheet, together with the micro-structure of the unchanged and the corroded metal.

x 1

a. Surface appearance of a corroded Muntz metal rod at the point at which failure occurred.



x 2

b. Longitudinal and cross-sections of the rod "a" near the point of failure. The outer layer resembled copper in color, it was brittle and could be readily cut with a knife; both α and β constituents had been "dezincified." The light colored center is the uncorroded alloy.

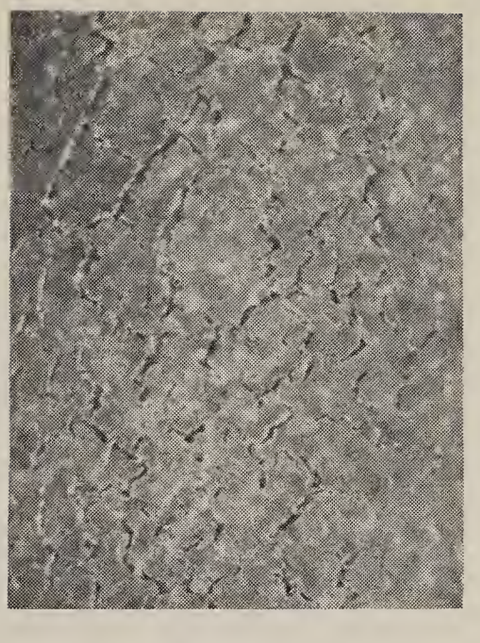
x 500

c. Micro-structure of the metal of a corroded condenser tube of Muntz metal, showing partial attack of the β constituent at the point examined. Etched as in "b."

Fig. 2. Wrought Muntz metal, after corrosion.

x 1½

a. Appearance of a lead cable sheathing which developed intercrystalline brittleness by corrosion in service, approximate composition, tin 1.09; lead 98.3 percent.

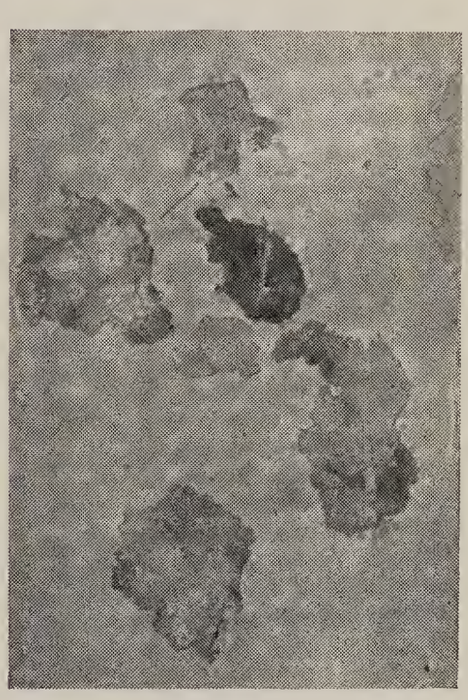


x 5

b. Surface appearance of a sheet of high-grade lead (99.99 per cent) after immersion of 24 days in a solution of *N* lead acetate and 0.8*N* nitric acid and bent at a slight angle. An intercrystalline brittleness resulted from the corrosive attack.

x 8

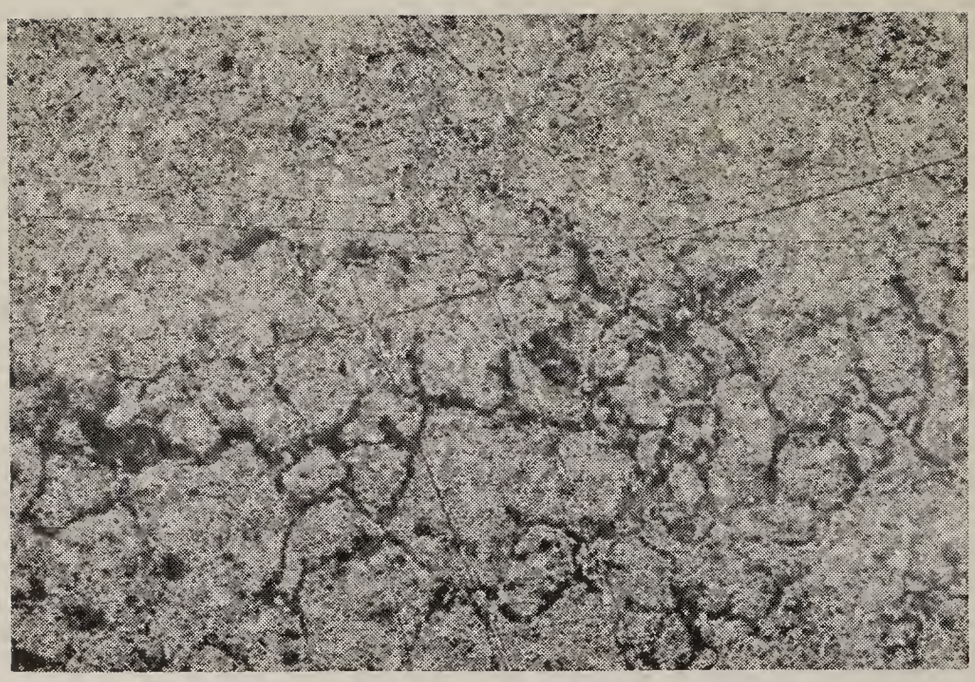
c. Crystals which were detached from a sheet of commercial lead (lead 99.72; antimony, 0.07; iron, 0.02; tin, 0.14 percent) immersed for 4 days in an acidified solution of lead acetate (400 g. lead acetate, 100 cm.^{3} nitric acid, 1,000 cm.^{3} water). The corrosion of the lead was intercrystalline in nature.



x 8

d. Some of the crystals of "c" flattened out. Each crystal retained the characteristic malleability of lead, although the sheet as a whole was brittle.

FIG. 3. Appearance of lead after accelerated corrosion, and of commercial lead which corroded in service.



x 50

e. Cross-section of specimen "a," unetched. The lower edge of the micrograph coincided with the outer surface of the sheath The corrosive attack of the metal was intercrystalline in its nature.

FIG. 3.—*Continued.* Appearance of lead after accelerated corrosion, and of commercial lead which corroded in service.

x 1

a. Longitudinal section of a "safety" plug, to the deterioration of which was attributed the explosion of a marine boiler with considerable loss of life. The filling of tin was changed almost completely by service conditions into a hard refractory mass of tin oxide; a few globules of tin may still be seen in the interior.

x 2

b. Portion of "a" after polishing the surface. The white areas are globules of tin which fused when the plug became overheated. The greater part of the filling consisted of tin oxide which because of the infusibility caused the explosion of the boiler.

FIG. 4. Structure of safety boiler plugs which deteriorated in service.

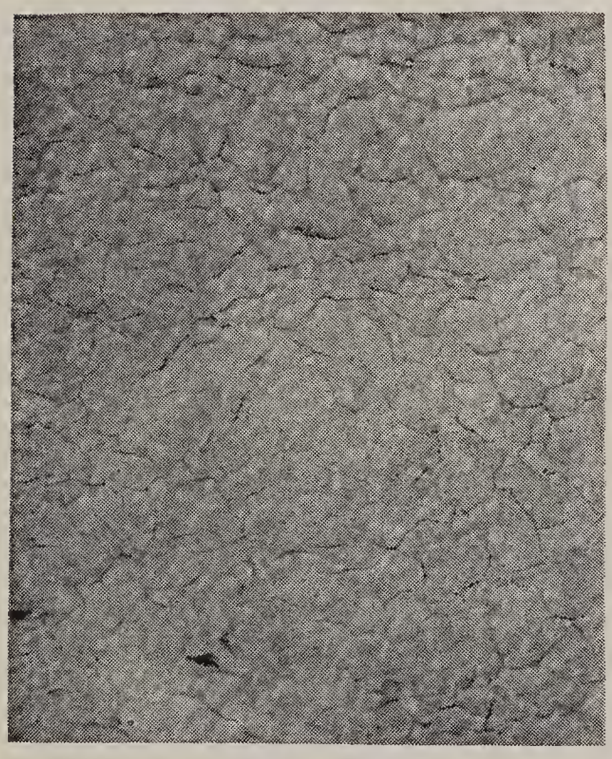
c. Longitudinal section of a plug used for four months, the tin filling of which has begun to deteriorate. The oxidation of the tin has occurred by the formation of a tree-like network permeating the tin, a considerable increase in volume of the tin filling has occurred. Specimen is unetched.

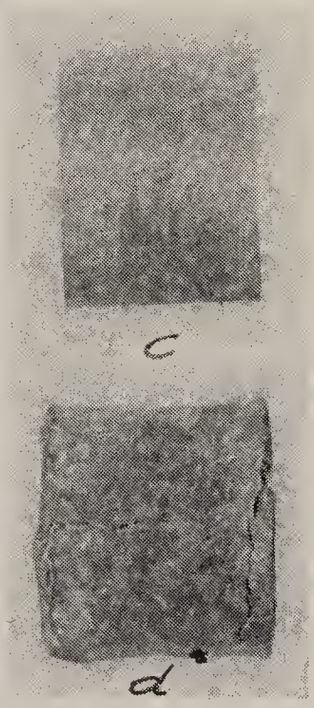
x 1

FIG. 4—*Continued.* Structure of safety boiler plugs which deteriorated in service.

x ¼

a. Fuse box cover, approximate composition: aluminum, 15; lead, 0.4 percent, zinc remainder, which was used in a tropical climate. The cast alloy warped and hardened in service.





c. Cylinder of an alloy, composition: copper, 1.4; aluminum, 15.2; zinc, 83.4 percent, exposed to "dry heat" (100° C.) for 6 days. The dimensions of the specimen remained unchanged.

d. Specimen similar to "c" exposed to "moist heat" (100° C.) for 6 days. The specimen expanded and cracked.

x 1

b. Surface of specimen "a," showing "alligator cracks"

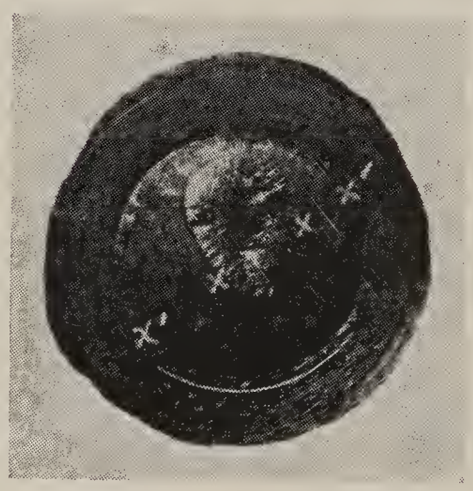
x 1½

FIG. 5. Appearance of certain aluminum alloys of high zinc content, after deterioration.

x 100

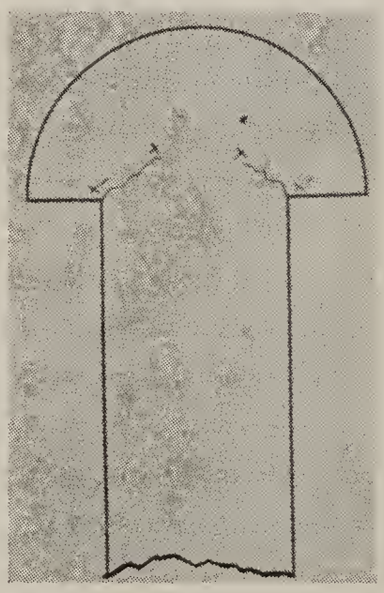
e. Cross-section of specimen similar to "d," showing the "expansion cracks" which formed in the metal near the surface by the action of heat and moisture; most of these occur in the eutectic; the specimen was unetched.

FIG. 5—*Continued.* Appearance of certain aluminum alloys of high zinc content, after deterioration.



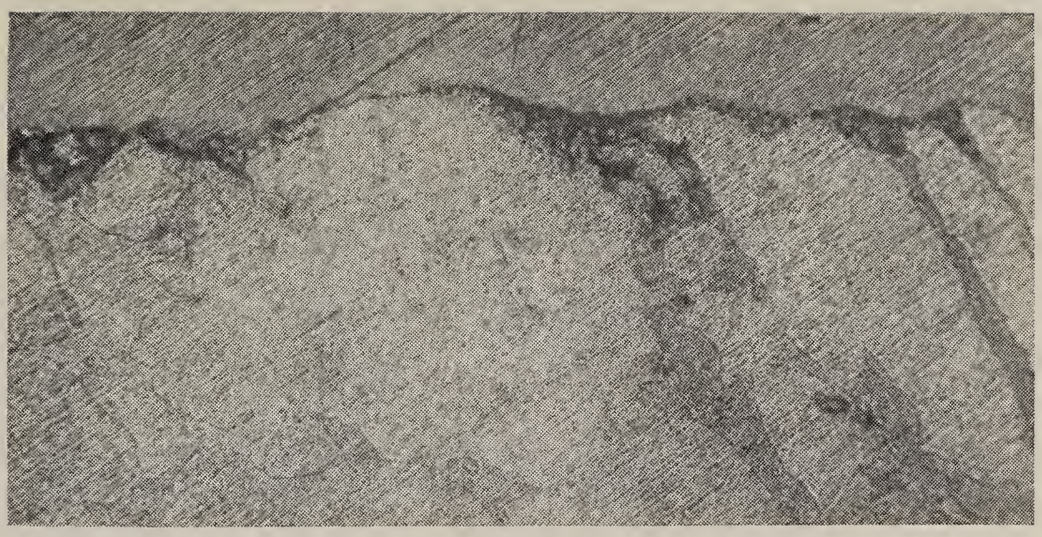
x 1

a. Fractured face of the bolt head which dropped off "of its own accord."



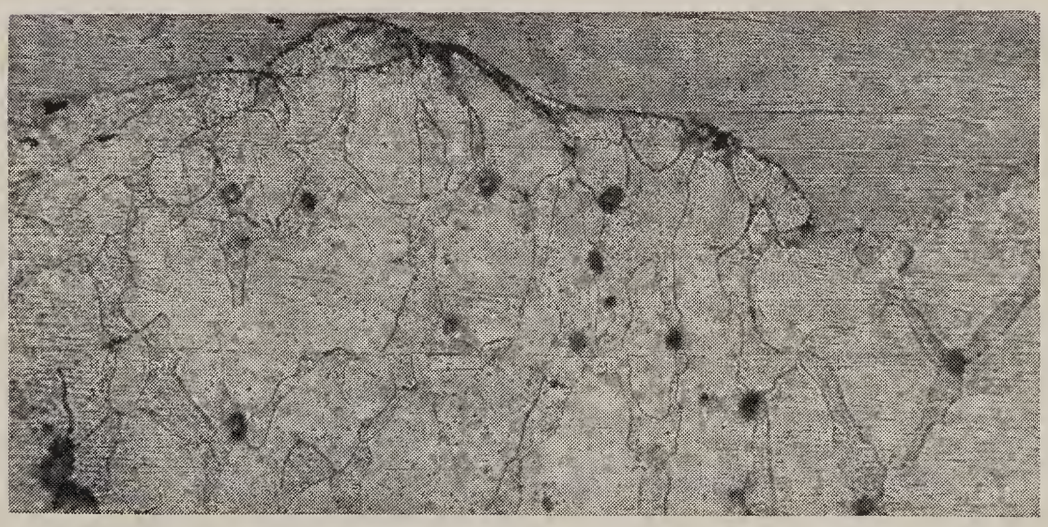
b. Longitudinal section of the bolt just before the head was detached.

FIG. 6. Structure of a brass (Muntz metal) bolt which failed in service, evidently by being corroded while stressed in tension.



x 250

c. Micro-structure of the metal at the fracture in the portion x--x′ of "a" and "b." The constituent has been dezincified by the corrosive action of the sea water to a considerable depth (black in micrograph) by corrosion.



x 250

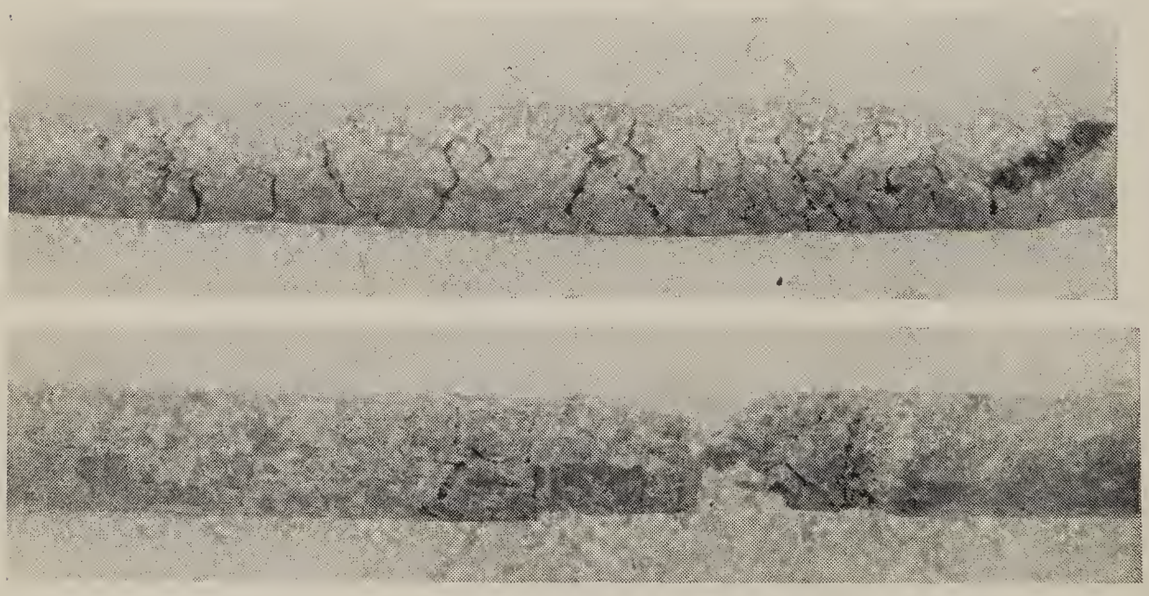
d. Micro-structure of the metal at the fracture in the central portion, x--x in "a" and "b." No selective corrosion has occurred here, tensile stress alone caused the fracture of the part. Etching reagent, ammonium hydroxide, followed by oxidation in air.

FIG. 6—*Continued.* Structure of a brass (Muntz metal) bolt which failed in service, evidently by being corroded while stressed in tension.

x 250

Fig. 7. Micro-structure of corroded Muntz metal, illustrating the effect of stress in localizing the corrosive action of this alloy.

A tensile specimen, ¼ inch diameter encircled by a sharp narrow V-groove, was immersed in a 5 percent solution of sodium chloride while under stress. The micrograph shows a section of the metal at the apex of the groove. Dezincification of the β constituent appears to have been accelerated by the relatively higher stress at the apex of the groove. Etching reagent, ammonium hydroxide containing ammonium persulphate.



x 3

Fig. 8. Appearance of specimens of lead stressed in tension while being corroded. The specimens of lead (99.99 percent purity) were surrounded by a solution of N lead acetate containing $N/2$ nitric acid and subjected to a tensional stress of 450 lb./sq. in. which was one-fourth of the breaking strength of the material as ordinarily determined, 1,790 lb./sq. in.

a (above). Appearance of specimen after 15 days' immersion.

b (below). Similar specimen, broken after an immersion of 20 days.

stressed specimen was surrounded by a solution of *N* lead acetate acidulated with *N/2* nitric acid. The metal, though inherently ductile, behaved as a brittle material and intercrystalline fissures were readily produced. Fig. 8b shows a similar specimen after a similar fracture resulted under these conditions.

III. SUMMARY.

The foregoing cases of non-ferrous corrosion have been chosen as types to illustrate a few of the many forms in which failure by corrosion may occur. It is quite evident that a measure of the corrosion, either by the mere loss or gain in weight, as the case might be, would be of very little moment in demonstrating the extent to which corrosion had progressed and the seriousness of the attack in any of the cases discussed. Although the four illustrations have been described as distinct types for convenience, it is quite evident that they are distinct types only so far as appearance is concerned. Fundamentally, they are all very similar.

DISCUSSION.

F. N. Speller[1]: I would just like to call attention to another aspect of the alloy corrosion that is of some practical importance, and that is, the de-zincification of brass pipes and tubes in water conduits and condensers. Sometimes a brass tube will go very rapidly, that is, in five or ten years, under hot water conditions; at other times they will last a long time. I just wish to suggest this as a subject for investigation. We have found that the oxygen content of the water, here again as in the case of iron, has an important influence on the deterioration of alloys. The reaction is not exactly the same as in the case of iron corrosion, but the practical results, by the depolarizing of the surface of the metal with the oxygen dissolved in the water, are the same. The difference as in the case of iron is very marked, indeed, so much so that in most cases you get no corrosion of brass and zinc alloys in the absence of the oxygen, and in many cases very

[1] Metallurgical Engineer, National Tube Co., Pittsburgh, Pa.

rapid corrosion if oxygen is present. Where free mineral acid is present corrosion will of course occur in the absence of oxygen.

CARL L. FINEMAN[2]: Though the phenomenon is only remotely connected with the regular corrosion, I would like to ask the numerous experts present for an explanation of the cause for the failure of a cast iron acid egg. The egg had been used for some time, as far as I recollect, about 6 months, for handling mixed nitration acids containing some excess of SO_3 and had been cleaned at least one time, showing no appreciable signs of corrosion.

One night, after working-hours, nitrous fumes were detected and traced to the acid egg, which was buried in the ground. Upon investigation it was found that the egg was cracked. The shape of the crack reminded me of the shape of a tear produced in a piece of cloth.

The material of the egg was examined and was found to be a good grade of cast iron. The interior of the egg showed no appreciable signs of corrosion.

Our conclusion at the time was that the failure must have been due to the release of some inner strain produced in cooling. Since that time I have read about similar experiences in English munition factories. It seems as if the phenomenon would occur only when highly concentrated acids such as those used in the manufacture of high explosives are transported in the egg.

I might add that the egg had been used at a pressure of about 35 lb. per sq. in. about three hours before the crack was detected. At that time no leakage of acid fumes was observed.

C. H. DESCH[3]: (*Communicated*): Mr. Rawdon's experiences in regard to corrosion are very similar to those of others who have worked on the subject. I agree with him entirely in laying stress on the microscopical study of the conditions under which corrosion takes place, the results being far more valuable than those of experiments in which the loss of weight of metals and alloys on exposure to various corroding agents is determined.

[2] Chemical Engineer, Stockholm, Sweden.

[3] Professor at University of Sheffield, England.

In a series of papers by Mr. S. Whyte and myself,[4] it has been shown that corrosion is largely dependent on the physical characters of the corrosion product, and this has been amply confirmed by the extensive researches of the Corrosion Research Committee of the Institute of Metals.[5] As an instance of the utility of microscopical investigations, reference may be made to the fact mentioned on p. 229, that the removal of zinc from Muntz metal by sea-water is prevented by the presence of 0.5 percent of tin in the alloy. This is not easily explained on electrochemical principles, the lowering of the solution pressure by tin being far too small to account for the great effect. Our experiments showed that the reason was a mechanical one.

In the initial stages, corrosion was even slightly accelerated in the presence of tin, but this metal formed an oxychloride with the salt in the water, and this corrosion product had the peculiar property of forming an adherent layer, which protected the surface of the metal as a layer of varnish would do. Several other peculiarities of corrosion may be accounted for by the production of such layers, which may be protective, as in this case, or may tend to collect in isolated masses which accelerate corrosion, as in the case of copper oxychloride on brass tubes.

The intercrystalline brittleness of lead, caused by immersion in certain solutions, occurs with pure assay lead foil as well as with commercial sheet. It has recently been shown by A. Thiel[6] that this separation of lead into grains takes place only when the solution contains nitric acid or nitrates. It may be remarked that corrosion usually tends to advance into a metal along the crystalline boundaries. Our work has shown that when salt water attacks alpha brass, zinc is removed first along the boundaries of the grains, so that a border of copper is found enclosing the grains even at a considerable depth below that to which the general corrosion has penetrated. The deterioration of tin plugs described by Burgess and Merica is, no doubt, of a similar character, the oxidation advancing along crystal boundaries. The penetration of oxygen into iron and nickel, and

[4] Journ. Inst. Metals, 1913, **10**, 304; 1914, **11**, 235; 1915, **13**, 80; **14**, 189; Trans. Faraday Soc., 1916, **11**, 198.

[5] Journ. Inst. Metals, 1919, **21**, 37; 1920, **23**, 65.

[6] Ber. deutsch. chem. Ges., 1920, **53**, 1052.

of hydrogen into iron, follows the same course. It is curious that where the crystal grains are twinned, twin boundaries may often behave like true boundaries, corrosion following them both. We have observed this especially in brass condenser tubes.

The relation between applied stresses and the initiation of corrosion is an important one, and recent work in this country has shown that slight corrosion of cold-worked metals may play an important part in what is known as "season cracking." Papers

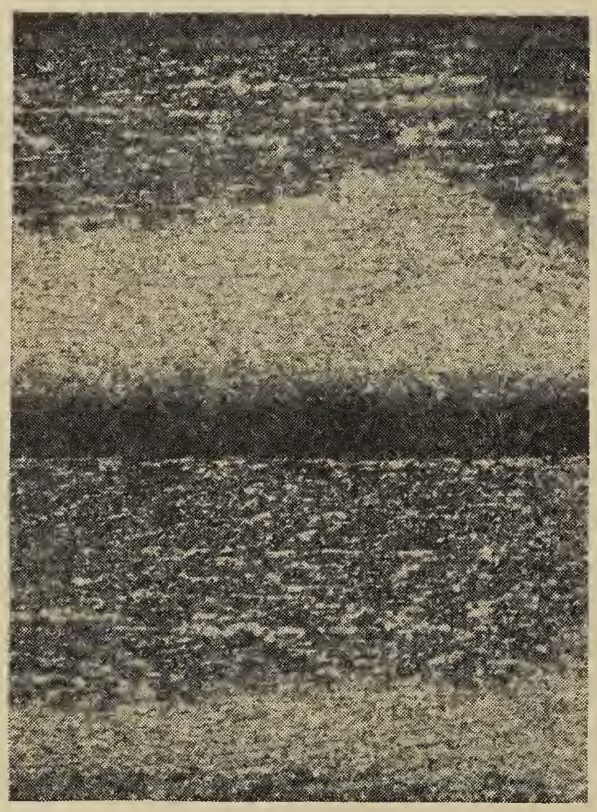


FIG. 1. Edge section of a corroded Muntz metal condenser tube analyzing copper, 61.17%; lead, 0.22%; iron, 0.04%; zinc, remainder.
Etch $NH_4OHH_2O_2$ Mag. x25

FIG. 2. Same specimen as Fig. 1, but Mag. x75.

published by the Bureau of Standards relating to the failure of metal parts in the Catskill aqueduct also contain important information on this point. It is satisfactory to observe the tendency, in papers by Mr. Rawdon and his colleagues, to consider in detail the physical and mechanical factors in corrosion. It is rarely possible to predict the behavior of a metal or alloy towards corroding agents from electrochemical considerations alone, since the surface is altered from the first moment of the process, and its subsequent course depends on the nature of the process prod-

FIG. 3. Longitudinal section of cracked brass wire which had been bent and kept under tension. Analysis: Copper, 64.18%; lead 0.012%; iron, 0.02%; zinc, remainder.
Etch $NH_4OHH_2O_2$ Mag. x75

FIG. 4. Same wire as Fig. 3, but bent at a greater angle. Note that the cracks are proportional to the strain.

uct and on the adhesion or detachment of the solid portion of that product, involving a complex series of events, which may best be followed by means of the microscope.

W. B. PRICE[7] (*Communicated*): Mr. Rawdon is to be congratulated for presenting in such a clear form the various types of non-ferrous corrosion. This subject is of vital importance to those in the brass industry, and we appreciate any investigations which help to solve our problems.

Several examples of non-ferrous corrosion have come to my attention which confirm Mr. Rawdon's observation, and may be of interest to the other members. Figures 1 and 2 illustrate the microstructure of a corroded Muntz metal condenser tube and are examples of the selective attack of one of the constituents (beta) of a duplex alloy.

The simultaneous action of stress and corrosion is illustrated by micrographs shown in figures 3 and 4, which represent the structure of a brass wire used in the construction of a "dandy" roll. The hard drawn wire, after being bent at an angle, is held in tension and is attacked by the action of the chemicals at the point where the stress is greatest. In this case the metal is broken down at the crystal boundaries to a great extent by the magnitude and the distribution of the stresses existing in the material. It is noteworthy to mention that the failure in this case is very similar to so-called season cracking.

W. H. BASSETT[8] (*Communicated*): Mr. Rawdon's paper is very complete and it hardly seems possible to discuss it. He has stated the facts of the case very clearly and they are entirely according to our experience.

[7] Chief Chemist and Metallurgist, Scovill Mfg. Co., Waterbury, Conn.
[8] Technical Supt. and Metallurgist, The American Brass Co., Waterbury, Conn.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

ELECTROLYTIC CORROSION OF LEAD BY CONTINUOUS AND PERIODIC CURRENTS.[1]

By E. R. Shepard.[2]

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1. INTRODUCTION.

In 1916, McCollum and Ahlborn made a study of the influence of frequency of reversal of current on electrolytic corrosion, and published the results in Technologic Paper No. 72 of the Bureau of Standards. The conclusions drawn from this study were briefly given as follows:

1. The corrosion of both iron and lead electrodes decreases with increasing frequency of reversal of the current.

[1] Manuscript received January 31, 1921.
[2] Electrical Engineer, Bureau of Standards.

2. The corrosion is practically negligible for both metals when the period of the cycle is not greater than about five minutes.

3. With iron electrodes a limiting frequency is reached between 15 and 60 cycles per second, beyond which no appreciable corrosion occurs. No such limit was reached in the lead tests, although it may exist at a higher frequency than 60 cycles.

4. With periodically reversed currents, the addition of sodium carbonate to the soil reduces the loss in the case of iron and increases it in the case of lead.

5. The coefficient of corrosion of lead, under the soil conditions described in the report, when subjected to the action of direct current was found to be only about 25 percent of the theoretical value.

6. The corrosion of lead reaches practically the maximum value with a frequency of reversal lying between one day and one week.

7. The corrosion of iron does not reach a maximum value until the period of the cycle is considerably in excess of two weeks.

8. The most important conclusion to be drawn from these investigations is that in the so-called neutral zone of street railway networks where the pipes continually reverse in polarity, the damage is much less than would be expected from a consideration of the arithmetical average of the current discharged from the pipes into the earth. Where pipes are alternately positive and negative with periods not exceeding 10 or 15 minutes, the algebraic sum of the current discharged in and out is more nearly a correct index to the total damage that will result than any other figure that can readily be obtained.

9. The reduction in corrosion due to periodically reversed currents appears to be due to the fact that the corrosive process is in a large degree reversible; so that the metal corroded during the half cycle when current is being discharged is in large measure re-deposited during the succeeding half cycle when the current flows toward the metal. The re-deposited metal may not be of much value mechanically, but it serves as an anode surface during the next succeeding half cycle, and thus protects the uncorroded metal beneath.

10. The extent to which the corrosive process is reversible depends upon the freedom with which the electrolyte circulates, and particularly, on the freedom of access of such substances as oxygen or carbon dioxide, which may result in secondary reactions giving rise to insoluble precipitates of the corroded metal. It is largely for this reason that the corrosion becomes greater with a longer period of the cycle, since the longer the period the greater will be the effect of these secondary reactions.

Some of these conclusions, particularly 2, 5 and 9, have seriously been questioned. The low coefficient of corrosion of lead under continuous current, as found by McCollum and Ahlborn, seemed to require further study along this line, particularly as only a few tests were made on lead, the principal work involving a study of corrosion of iron. Moreover, the tests were made with symmetrically reversed currents with the algebraic average equal to zero in all cases. A further study with unsymmetrical currents with algebraic averages greater and less than zero seemed desirable. The theory advanced in conclusion 9 relative to the re-deposition of metal under reversed current electrolysis has not been generally accepted, and this also needed further study. The subject was accordingly taken up again in 1919, the intention at first being to make tests on lead cables installed on the grounds of the Bureau in a manner similar to that found in practice. After a thorough discussion of the proposed tests with some of the owners of lead sheathed cables it was decided to continue first the tests in the laboratory where the conditions could be more accurately controlled, after which the field measurements could be made if a further investigation seemed needed. The reversing commutator used by McCollum and Ahlborn was modified in such a manner as to give various irregular waves with different frequencies. Lead specimens only were tested in the investigation, and as far as possible, the same methods employed as formerly. All tests were made at room temperatures. Commercially pure lead taken from the sheath of a large power cable was used in all tests.

In view of the fact that lead cables are often found in manholes and conduits containing water, it was thought best to conduct the tests with specimens submerged in tap water as well as in earth. The greater chance for migration of the ions in the solution due

to convection currents which would decrease the chance for redeposition of metal, make the two conditions very different under reversed current electrolysis, and for this reason practically all tests were made in both water and earth.

2. CORROSION BY CONTINUOUS CURRENT.

(a) *Variation of Coefficient of Corrosion with Current Density:* In the discussion which followed the presentation of McCollum and Ahlborn's paper before the New York Section

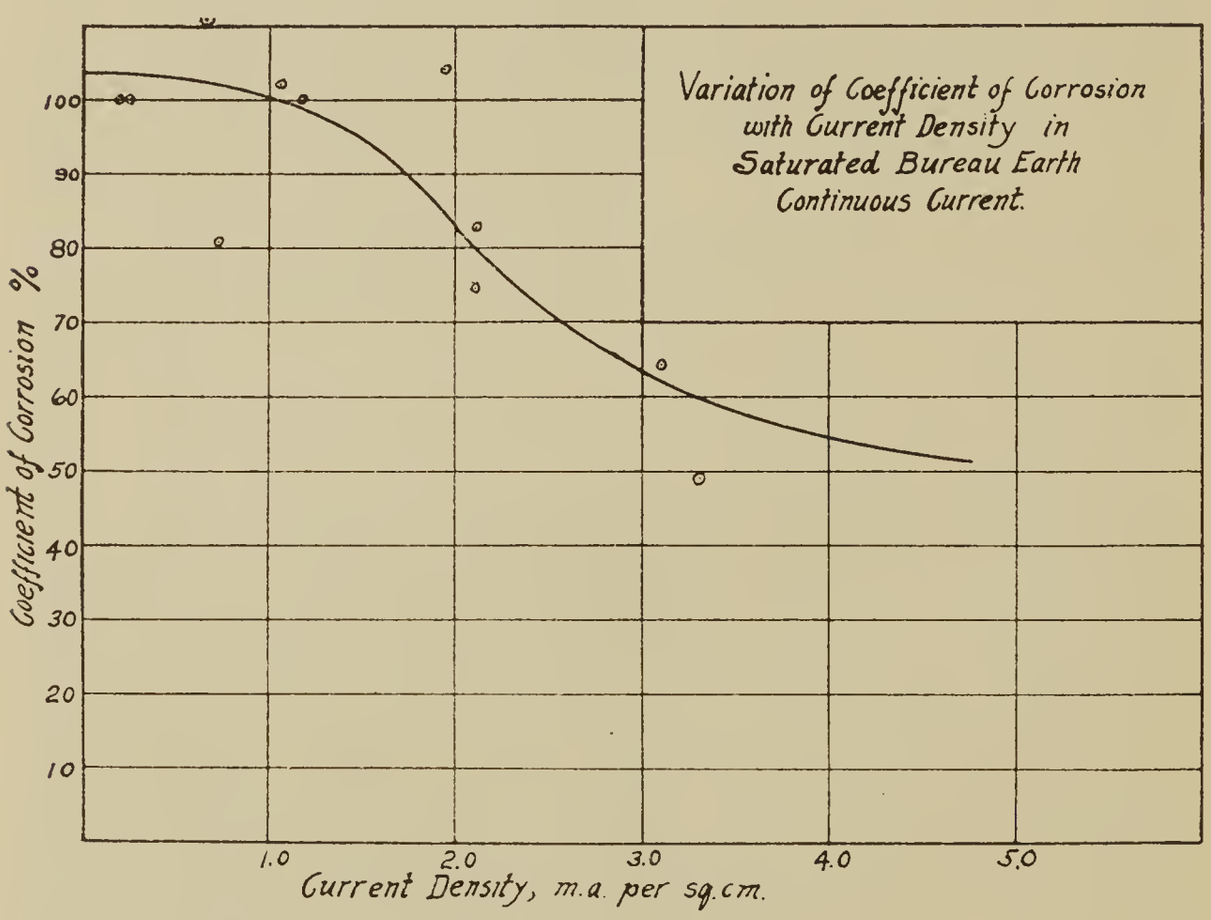


FIG. 1.

of the American Electrochemical Society and the American Institute of Electrical Engineers, reference was made to former work of the Bureau of Standards in which low coefficients of corrosion were obtained with relatively high current densities, and this was offered as an explanation for the low coefficients of corrosion[3] of lead by direct current. Early experiments of the Bureau had shown that in the case of iron a coefficient of corrosion of one

[3] Coefficient of corrosion is defined as the ratio of the actual corrosion observed to that which would have occurred if all of the electrode reactions determined by Faraday's law had been involved solely in corroding the anode.

hundred percent is obtained with current densities even greater than 0.5 milliampere per square centimeter (0.46 amp. per sq. ft.), the value used by McCollum and Ahlborn, but no corresponding tests had been made with lead. Accordingly, a series of measurements were made with direct currents of various densities to determine the relation between the coefficient of corrosion and the current density. The results of these measurements are shown in Fig. 1, where it will be seen that with current densities not ex-

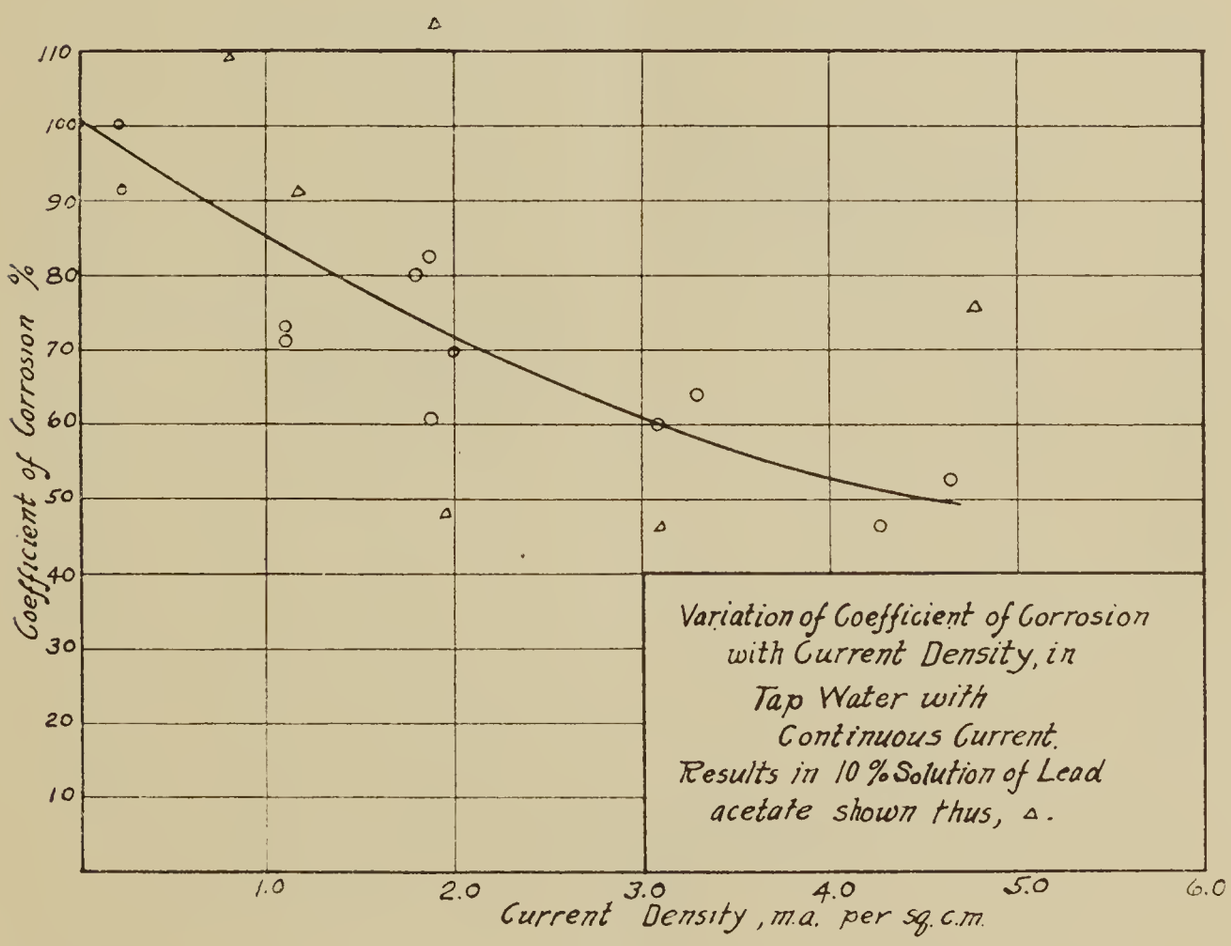


FIG. 2.

ceeding 1 milliampere per square centimeter (0.93 amp. per sq. ft.), the coefficient of corrosion reached 100 percent or over. These tests were made in earth from the Bureau grounds highly saturated with tap water, and also in tap water alone. The results of the latter are shown in Fig. 2. With tap water the coefficient of corrosion drops off rapidly as the current density increases, but with very low densities a 100 percent coefficient was found. With high-current densities ranging up to 5 milliamperes per square centimeter (4.6 amp. per sq. ft.), the coefficient decreases in

both earth and water, reaching a minimum value of about 50 percent. As a current density of 0.5 milliampere per square centimeter appeared to give the full theoretical amount of corrosion, this value was used in practically all other tests where other variables were under investigation. The apparent super-corrosion in earth under some conditions is probably the result of removing some lead during the cleaning process. In the case of tap water, the immediate decrease in the coefficient of corrosion from very

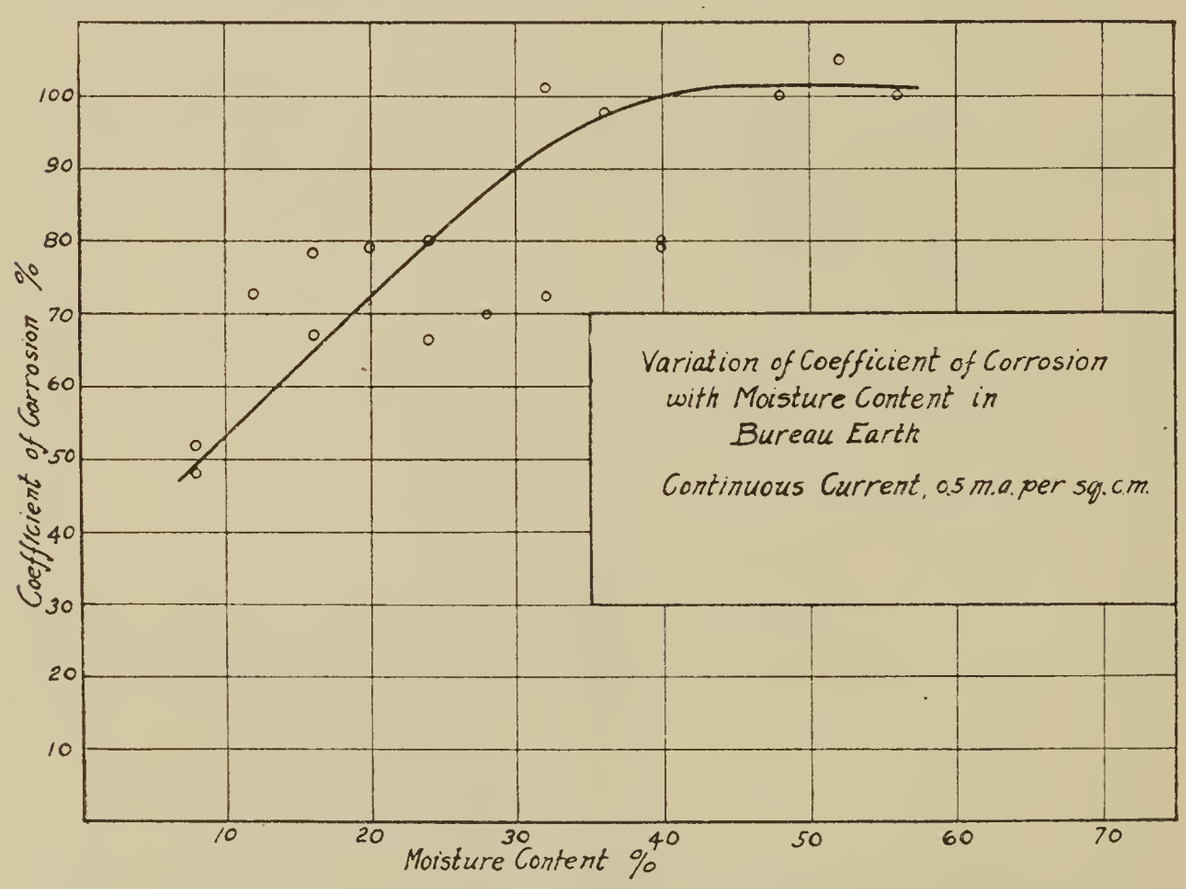


Fig. 3.

low current densities is not altogether clear but has been ascribed by electrochemists to the accumulation of the products of corrosion on the plates or in the electrolyte, thereby resulting in the evolution of gas rather than electrolysis of lead.

(b) *Variation of Coefficient of Corrosion with Moisture Content:* Fig. 3 shows the relation between the coefficient of corrosion and the percentage of moisture in Bureau earth. For moisture contents in excess of about 40 per cent. of the weight of the dry earth, which represents almost a saturated condition, the coefficient reaches the theoretical maximum or 100 percent. Below 40 per-

cent of moisture the coefficient drops off rapidly to about 50 percent, for the driest earth that will readily conduct current. The values shown in this curve were obtained in earth samples which were tightly tamped around the test specimens. Preliminary experiments in which the earth was pressed into jars but not tamped gave much lower coefficients of corrosion and check the work done by McCollum and Ahlborn, who found a maximum coefficient of only about 25 percent with continuous current under approximately similar conditions

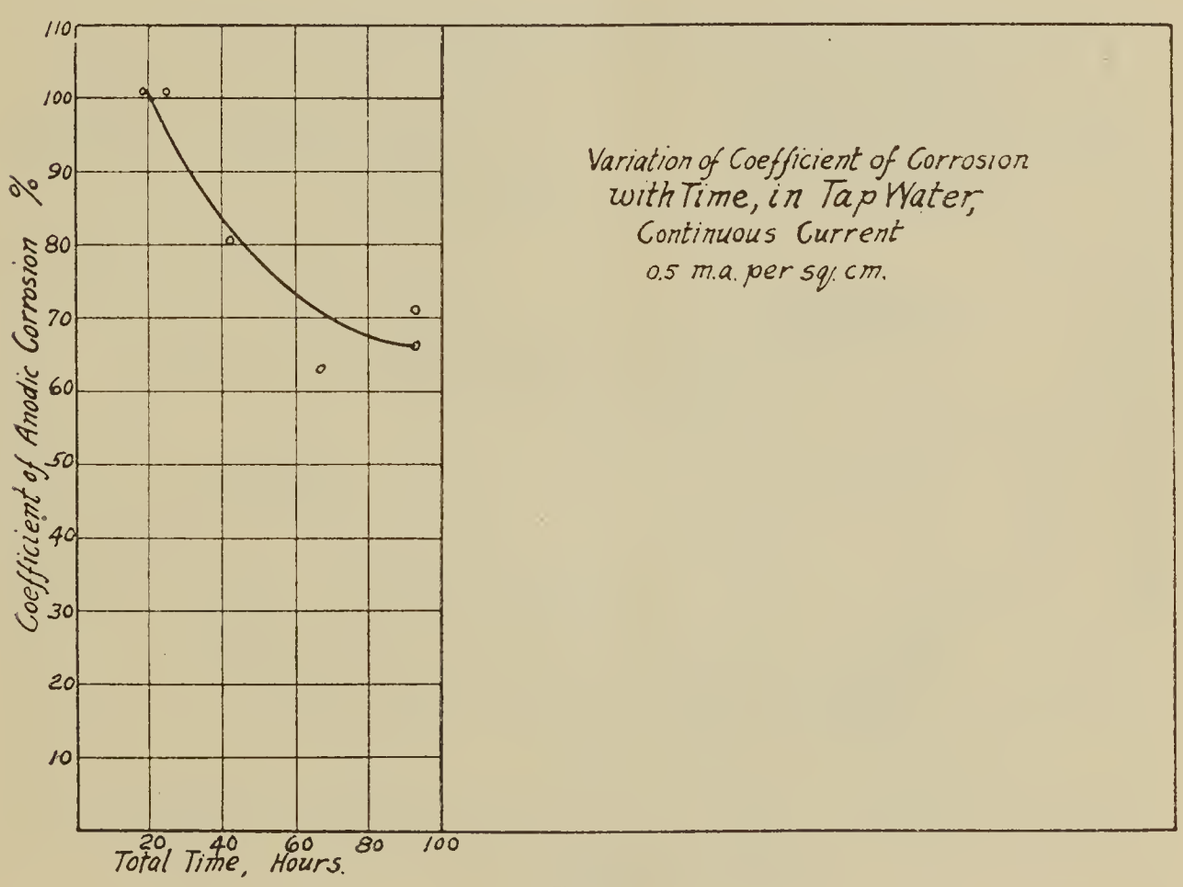


FIG. 4.

For all tests involving other variables a thoroughly saturated earth was employed.

The cause for the low coefficient in dry earth is probably to be found in the imperfect contact between the metal and the earth, thus leading to high current densities at points. The fact that the lowest values observed, about 50 percent, correspond closely with the lowest values obtained with high current densities bears this supposition out. Moreover, the appearance of the plates after test in relatively dry soils show very uneven corrosion with excessive pitting at points. Outdoor tests with continuous current

were made on four lead plates 7.1 cm. by 9.5 cm., connected in parallel. A current density of 0.28 milliampere per sq. cm. was used and this continued for about nine days. The soil was wet down at the time the electrodes were buried and was very damp throughout the period of the test. The total loss observed was 121.84 grams and the total ampere hours 135.3. The calculated coefficient of corrosion is 90 percent.

(c) *Variation of Coefficient of Corrosion with Time or with Total Ampere-Hours:* This relation in the case of lead specimens

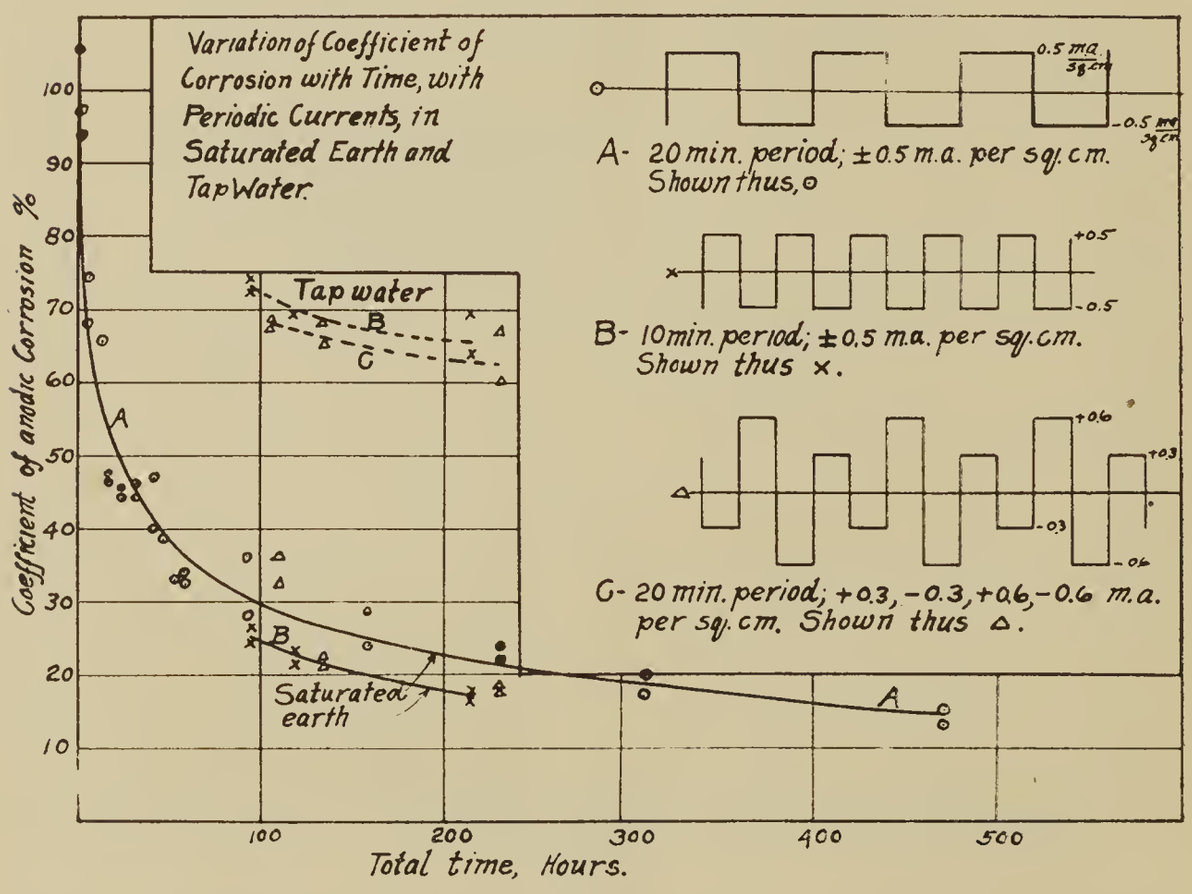


FIG. 5.

in tap water with a current density of 0.5 milliampere per square centimeter is shown in Fig. 4. The coefficient is seen to drop from 100 percent after about 20 hours to about 65 percent at 90 hours. The reason for this is probably due to the same cause as the decrease in the coefficient with increasing current densities. Similar tests were made with specimens in earth, but no appreciable decrease in the coefficient with time was observed up to 300 hours with a current density of 0.2 milliampere per square centimeter (0.23 amp. per sq. ft.).

3. PERIODICALLY REVERSED CURRENTS.

In this series of measurements all calculations of coefficient of corrosion were made on the basis of anodic current.

(a) *Algebraic Average Equal to Zero, Variation of Coefficient with Time:* Referring to Fig. 5, it is seen that with a twenty-minute period having equal positive and negative values and times, the coefficient of corrosion in earth decreases rapidly, reaching a value of about 14 percent at about 465 hours. This figure coin-

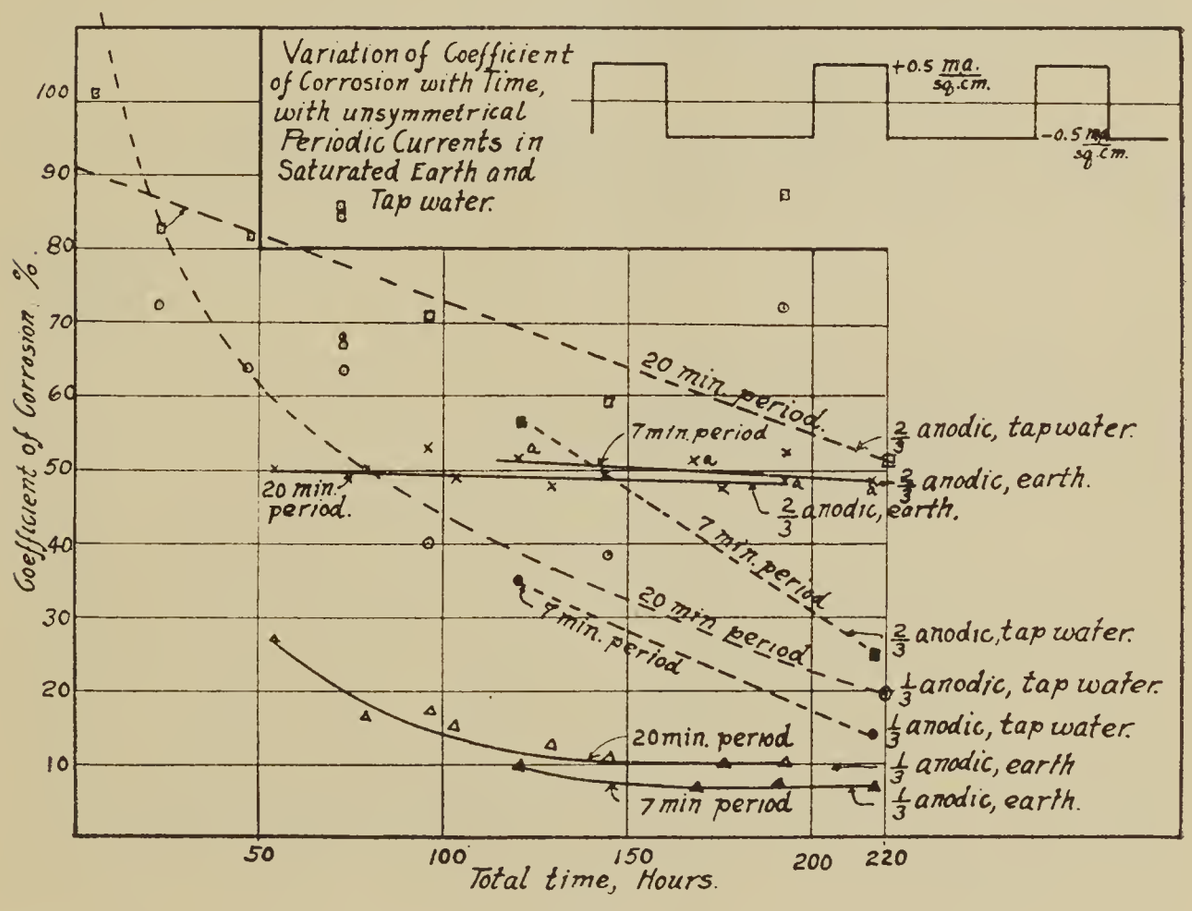


FIG. 6.

cides closely with those given by McCollum and Ahlborn for similar conditions. In the tap water the values are much higher but there is also a tendency to decrease with time. With a ten-minute period the coefficient in earth is slightly lower than with a twenty-minute period. Not enough tests were made in water to establish a difference between the ten- and twenty-minute periods. The irregular wave having a twenty-minute period with ten-minute reversals as shown in Fig. 5 gave about the same results as the simple ten-minute period. The presence of certain

lead salts in the electrolyte was found to greatly decrease the coefficient of corrosion.

A 48-hour test with a 20-minute period was made with a current density of 0.5 milliampere per square centimeter (0.46 amp. per sq. ft.) in which the following results were obtained:

	Coefficient of Corrosion Percent
Dry earth saturated with a 5 percent solution of lead nitrate	32.5
Dry earth saturated with a 5 percent solution of lead actetate	5.9
Tap water with 5 percent lead nitrate	36.7
Tap water with 5 percent lead acetate	37.1

With a two-hour period continuing for eight hours, with 1.0 milliampere per square centimeter (0.93 amp. per sq. ft.), the following results were obtained:

	Coefficient of Corrosion Percent
Earth with 5 percent lead nitrate	84.7
Earth with 5 percent lead acetate	22.5
Tap water with 5 percent lead nitrate	48.6
Tap water with 5 percent lead acetate	48.6

The small coefficients of corrosion obtained with these electrolytes having a greater concentration than normal soil or tap water, and therefore permitting of a reversing action with alternating currents, support the re-deposition theory. The decrease in the coefficient with time, and therefore with ampere hours, is easily explained by the increase in concentration of the lead ions in the electrolyte resulting from the continued action of the periodically reversed current.

(b) *Unequal Positive and Negative Values, Currents or Times:* The results of this series of tests are shown in Figs. 6 and 7. It will be seen that when the plates are anodic one-third of the time and cathodic two-thirds of the time, the coefficient drops to about 10 percent after 200 hours for a 20-minute period in earth, and to a slightly lower value for a 7-minute period. In tap water the coefficient is much higher than in earth, but shows a more rapid decrease with time, and would no doubt reach the earth values were the tests continued for a longer time. With equal times but current values in the ratio of 1 to 2, the results

are practically the same as for equal currents and unequal times. This is shown in Fig. 7.

Commutators were provided which gave positive and negative conditions in the following ratios: 1/9 positive and 8/9 negative, 1/3 positive and 2/3 negative, 1/2 positive and 1/2 negative. By measuring the corrosion loss on both specimens in the cells subjected to these unsymmetrical currents the reversed conditions were also secured, namely 8/9 positive and 1/9 negative, 2/3 posi-

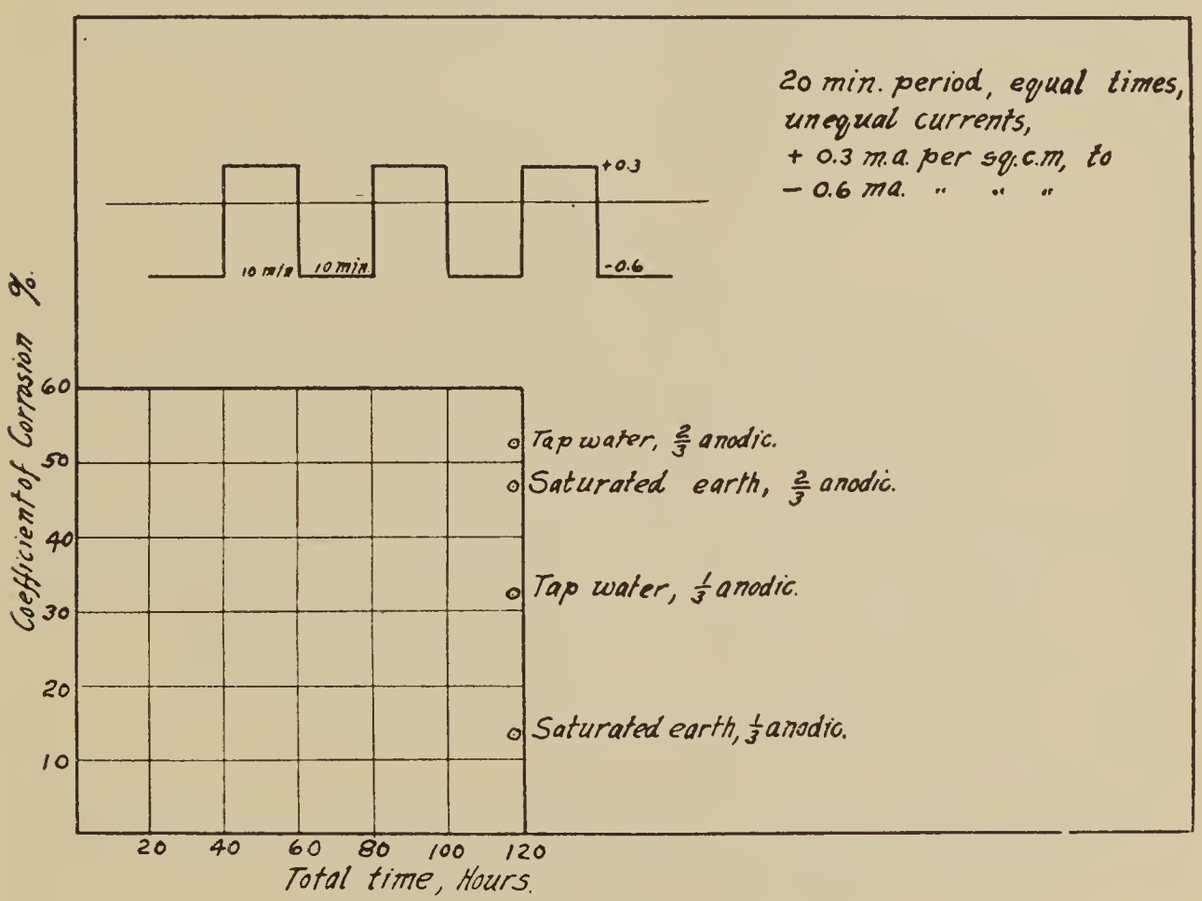


FIG. 7.

tive and 1/3 negative. A series of measurements was made under these five conditions as well as with continuous current and the results for a definite time, namely 100 hours, are plotted in Fig. 8. These curves show the coefficient of corrosion for different percentages of the total time the plates are anodic. The same relations would hold whether the unequal positive and negative values were obtained by varying the time or the magnitude of the positive and negative current.

(c) *Indications of Re-deposition of Lead Under Alternating Current Electrolysis:* The following phenomena observed during

these tests indicate that the low coefficients of corrosion obtained with periodically reversed currents are due to a re-deposition of lead during the cathodic period, or to a reduction process at the cathode which amounts to the same thing as it makes free lead available in some form for anodic corrosion during the succeeding half cycle before the solid metal can be attacked.

With fresh tap water or normal soil very few lead ions are present and consequently very little deposition of lead on the

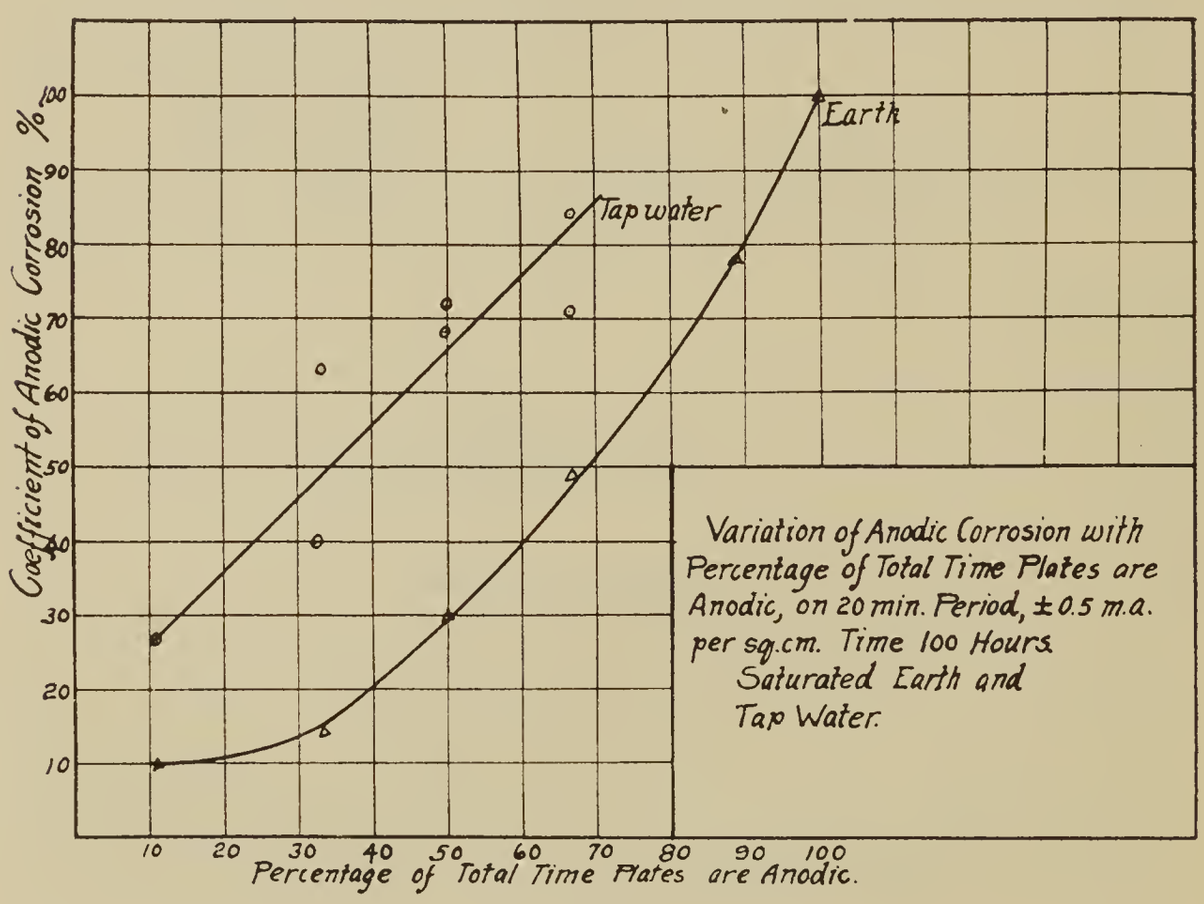


FIG. 8.

cathode is possible, consequently the anodic coefficient of corrosion approaches 100 percent. As the process goes on the electrolyte gradually increases in lead concentration, thereby permitting some deposition on the cathode with a consequent decrease in the coefficient of corrosion.

A few short time tests made with a 10 percent solution of lead acetate gave coefficients of corrosion of the order of 4 to 10 percent on a 30-minute period with equal positive and negative values, indicating that almost complete re-deposition was taking place.

The coefficient is lower in earth than in water, obviously due

to the fact that the products of corrosion are held in the soil close to the plate and are available for re-deposition during the cathodic period.

There is no indication that a negative condition or a reversing condition produces passivity which is the only other plausible explanation for the low coefficients observed under alternating current electrolysis.

Electrolysis of lead is a well-known reversible process as illustrated in the familiar Planté or lead storage battery action. Whether re-deposition takes place by a reduction process as in the lead storage battery or is deposited from lead salts present in the electrolyte is immaterial so far as the practical results are concerned.

4. CONCLUSIONS.

1. The results of these experiments agree generally with those obtained by McCollum and Ahlborn, with the exception, however, that in earth, under favorable conditions, with continuous current, a coefficient of corrosion of 100 percent was obtained. The low value reported by McCollum and Ahlborn was undoubtedly the result of using a lower moisture content than that employed in this series, and not tamping the earth around the electrodes.

2. With continuous current, the coefficient of corrosion in both tap water and earth decreases with an increase in current density, reaching a minimum of about 50 percent for current densities of 5 milliamperes per square centimeter. The theoretical maximum value of 100 percent was found for low-current densities of the order of 0.5 milliampere per square centimeter and less.

3. The coefficient of corrosion drops off rapidly as the moisture content of earth is decreased below the saturation point. For 40 percent moisture content and greater, if the earth is well tamped about the specimens, the full theoretical amount of corrosion occurs.

4. The coefficient of corrosion of lead in tap water decreases with time, but little or no decrease in the coefficient is observed with specimens in saturated earth.

5. With periodically reversed currents in which the anodic and cathodic conditions are equal, that is, when the algebraic average value of the ampere-hours is zero, the coefficient of corrosion

based on the anodic current, decreases rapidly with time, reaching a value of about 14 percent after 465 hours in saturated earth and about 50 percent in tap water.

6. The coefficient of corrosion increases with the percentage of the total ampere-hours contributing to an anodic condition.

A paper presented as part of a Symposium on Corrosion at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 21, 1921, Colin G. Fink in the Chair.

PRINCIPLES OF ALLOYING TO RESIST CORROSION.[1]

By Oliver P. Watts.[2]

Abstract.

A plea for intelligent use of metallography and metallurgical principles in attempts to find non-corrodible alloys. The general principle is laid down that the less corrodible alloys are either metallic compounds of simple chemical formula (which are apt, however, to lack malleability) or solid solutions of the more resistant metals in each other. The protective action of small amounts of one metal in another is described; an interesting test proving the protective action of copper in steel is given.—

[J. W. R.]

In recent years much attention has been given to the production of alloys designed to resist atmospheric and chemical corrosion. Some of the better-known products of this nature are tantiron, duriron, copper steel, stainless steel, monel metal and nichrome. In view of our knowledge of the chemical properties of the elements and the light which metallography has given us regarding the nature and constitution of alloys, it is surprising that the principles of alloying for protection have not already been clearly and fully set forth in the extensive literature devoted to the corrosion and protection of metals. This, however, does not appear to be the case. The new corrosion-resisting alloys seem to have been discovered entirely by trial, without any general principle to guide in the selection of the element or elements to be added to the metal which it is desired to render more resistant to corrosion.

It is not sufficient to add to the metal to be protected some other metal which is very resistant to corrosion, for instead of pro-

[1] Manuscript received February 15, 1921.

[2] Associate Professor, Chem. Eng., University of Wisconsin.

tecting, the addition frequently accelerates corrosion. This was shown a century ago by the experiments of Stodart and Faraday[3] in alloying several metals of the platinum group with steel. They say, "If two pieces, one of steel, and one of steel alloyed with platinum, be immersed in weak sulphuric acid, the alloy will be immediately acted upon with great rapidity and the evolution of much gas, and will shortly be dissolved, whilst the steel will be scarcely at all affected. In this case, it is hardly possible to compare the strength of the two actions. If the gas be collected from the alloy and from the steel for equal intervals of time, the first portion will surpass the second some hundreds of times."

It is easy to make a corrosion-resisting alloy from two metals which themselves are highly resistant, such as the noble metals, but the real problem is to take a cheap metal and add to it a small or a moderate amount of some other element that will render the resulting alloy resistant. Theoretical considerations would lead to the conclusion that of all the possible forms in which two elements alloy, the chemical compound will prove most resistant to attack. The truth of this is seen in the work of Moissan and his students in the making of new silicides and borides. He formed the desired compound in an excess of metal, which by boiling with acids was dissolved, leaving behind the chemical compound. But these same experiments show that it will not do to have both free metal and compound present in the alloy if it is to resist corrosion; the alloy must be all compound. For many uses of corrosion-resisting materials, malleability, or at least freedom from marked brittleness, is a necessity; but the brittleness of all ordinary chemical compounds is one of their most general characteristics, and the compounds formed between two metals are no exception to the universality of this rule. The use of alloys which are wholly compounds must be confined to places where brittleness is not fatal to their employment.

The protective effect of additions of copper and of nickel to iron has been known for several years. In seeking a reason for the protective effect of copper and nickel, in contrast to the accelerative effect of alloying platinum with iron, the writer found from published articles that both copper[4] and nickel form with iron,

[3] Trans. Royal Soc., 1822, 262.
[4] Trans. Am. Electrochem. Soc. (1912), 21, 358.

within the limits in which their addition is beneficial, solid solutions, *i. e.*, homogeneous substances in which neither metal can be detected by the microscope. Duriron, tantiron, etc., are iron-silicon alloys which contain about 15 percent of silicon. These are solid solutions, and exhibit remarkable resistance to corrosion. Monel metal, the natural alloy of nickel and copper, has found extensive application on account of its unusual resistance to corrosion by various chemicals; this also is a solid solution. One of the most important of the recent non-corrosive iron alloys is stainless steel, which is an alloy of iron with about 13 percent. of

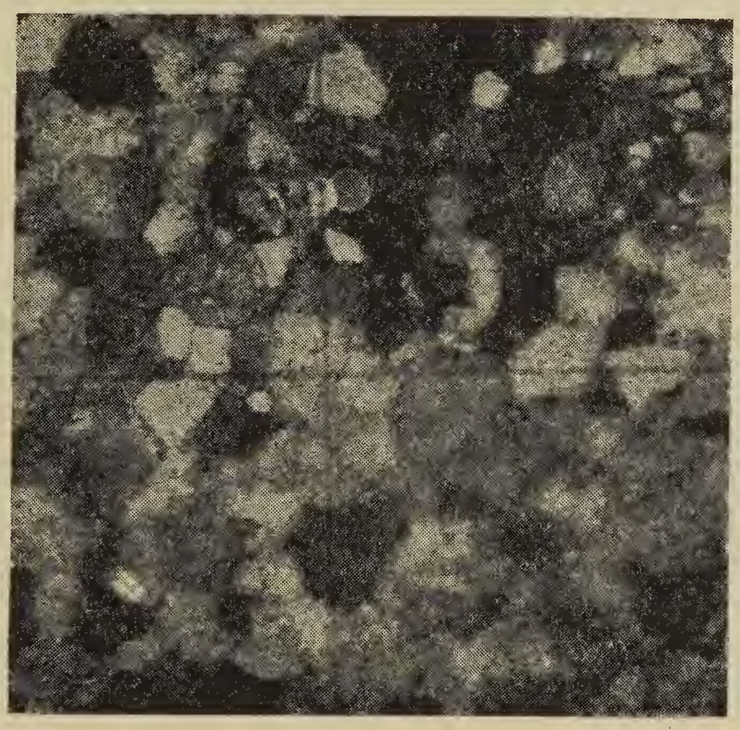


FIG. 1. Stainless Steel, Annealed—Magnified 100 Times.

chromium and 0.3 percent of carbon. Tammann and Trietsche[5] state that iron and chromium form a series of solid solutions, and the photograph of stainless steel shown in Fig. 1, for which the writer is indebted to E. D. Fahlberg, shows that the presence of a small percent of carbon does not alter this.

A consideration of the five corrosion-resisting alloys mentioned above leads to the conclusion that to increase the resistance to corrosion of any metal there should be alloyed with it another metal which is more resistant to corro-

[5] Zeit. anorg. Chem., **55**, 402.

sion, and which forms a solid solution with the metal whose resistance to corrosion it is desired to enhance.

That only a trace of the alloying element can produce remarkable effects is shown by "copper-steel." Two pieces, each 5 cm. square and of the same thickness, one of ordinary steel and the other containing about 0.25 percent of copper, were placed in 200 cc. of normal sulphuric acid for 20 hours at 30° C. The former lost 5.507 grams and was nearly all dissolved, but the latter lost only 0.063 gram in weight.

A test which the writer has found very useful for quickly distinguishing highly resistant alloys of iron is immersion for a couple of minutes in a strong and slightly acidified solution of copper sulphate. Only the most resistant alloys, such as duriron and stainless steel, fail to acquire a deposit of copper.

If the alloy specialist must have ductility in his alloy he is advised to experiment with metals more resistant to corrosion than the basic metal which he proposes to use, *i. e.,* metals below it in the electrochemical series in those electrolytes against whose attacks he desires it to be immune, and which form a solid solution with the basic metal. If brittleness is no detriment, he can hardly do better for resistance to acid solutions than to test various silicides of the metals.

Department of Chemical Engineering,
University of Wisconsin.

DISCUSSION.

H. S. Rawdon[1]: I had a question I wanted to ask Mr. Watts if he had been here concerning the micrograph shown on page 255. He states that it is stainless steel. Ordinarily we understand by that term steel of 13 percent chromium. He says "Tammann and Trietsche state that iron and chromium form a series of solid solutions." Recently we had occasion to examine practically all the commercial types of stainless steel, and all the chromium steels showed large amounts of carbide,

[1] Physicist, Bureau of Standards, Washington, D. C.

in fact, a prominent feature of the structure is the carbide of chromium and iron. The steels that are high in nickel are of the type of solid solution shown here in this Figure 1, and I was wondering if he had had this sample analyzed so that he knew exactly whether he was dealing with chromium steel or a high nickel steel. I am rather of the opinion he had a high nickel steel and did not know that he was working that type of material.

D. M. STRICKLAND[2]: I believe the author has presented thoughts which are of some value and should be considered when preparing rust resisting alloys. I have obtained certain of the alloys mentioned and have used them in work under my own observation, and the results of these tests show that I am not able to substantiate all the claims that Mr. Watts makes for his alloys. On page 255 his general conclusion is, that to increase the corrosion resistance of any metal, there should be alloyed with it in the form of a solid solution another metal which is more resistant to corrosion. He bases this conclusion on one experiment and one alloy. I took this same alloy and immersed samples in solutions other than the sulphuric acid mentioned, and obtained results which do not corroborate his statements. I believe Mr. Watts has not presented sufficient investigational data to warrant his comprehensive conclusions.

Time does not permit the presentation of a discussion which I have prepared, but when it is published in the Transactions you will find that the data submitted show that the alloy, the same as used by Mr. Watts, does not always conform to his own conclusion. (See below).

HENRY HESS[3]: Now, one matter indirectly raised is very far-reaching, it touches on the making of steel in a very important phase. With relatively few exceptions, new alloys are the result of cut-and-try methods rather than of logical developments; it is, therefore, entirely pertinent to ask for any guide or literature on the substances that will form solid solutions. If there is such a thing in existence I do not know it. If there is no such guide, the statement of the author regarding the formation of

[2] American Rolling Mill Co., Middletown, Ohio.
[3] Philadelphia, Pa.

solid alloys leaves each man to make his cut-and-try experiments as heretofore; there is, therefore, no value in that general statement to the steel maker. At the same time, if Mr. Watts or any other member present can contribute something along that line, he will contribute something that is really valuable to the industry, whether the contributing member is a university man or a man out of the industry, is a matter of indifference; undoubtedly, if the university man can contribute that thing, he will be doing a great deal for the standing that will be accorded to the university by the industry generally.

J. W. Richards[4]: To answer one of the points brought up by Mr. Hess, in Landoldt and Börnstein's Table (last edition), for instance, are given the fusing points, curves and the composition of a large number of binary alloys, not many tertiary alloys, and in these you would find some indication of which metals form solid solutions. In the books on metallography, such as Hoyt's or Gina's, there is more or less information in the diagrams as to which metals form solid solutions with others. In Bullen's book on steel there is considerable information about the relations of the other elements to steel, which form solid solutions and which do not.

Wm. M. Corse[6]: Before leaving this question of corrosion I should like to make a practical suggestion. It would be a very good idea if this Society expressed its interest in the subject of corrosion by asking the Division of Research Extension to work on this very interesting and valuable subject; and I would, therefore, move, if it meets with the approval of the chairman, that the Electrochemical Society at this meeting suggest to the National Research Council, through its Division of Research Extension, that the topic of corrosion be considered as an active and practical subject.

Colin G. Fink: It is needless to say that the Society will gladly support a movement of this kind. The matter will be handled through the regular channels at the next Directors' meeting. I should like to summarize the various points that have

[4] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.
[6] Gen. Mgr., Monel Metal Products Corp., Bayonne, N. J.

been brought out in this symposium in order that some of you, who have a hazy idea of what has been said, might get a clearer perspective. First of all, this symposium has emphasized that iron or steel containing about a quarter of one percent copper will withstand atmospheric corrosion better than iron or steel without copper. Secondly, iron and steel containing about a quarter of one percent copper, when completely immersed in ordinary tap water or slightly acidulated water, does not resist corrosion as well as pure iron does. Thirdly, in boiler practice and in hot-water systems, the presence of oxygen greatly accelerates corrosion, and the removal of oxygen from the boiler water practically eliminates corrosion. I think that point is pretty well established. Fourthly, similar to oxygen, carbon dioxide in boiler water derived from soluble iron bicarbonate, increases corrosion, and its removal practically eliminates corrosion.

Now as to the corrosion resistant alloys: All elements, such as chromium, silicon, nickel, etc., added to iron, tend to reduce corrosion, but detailed investigations are lacking. We are really just at the very beginning of that line of research. The corrosion of alloys is becoming of increasing importance, and although great progress has been made in recent years, the satisfactory co-ordination of results is lacking. So much for the points brought out in the symposium. As to suggestions for the future: First, we need more careful, more thorough investigation of the surface film, *e. g.*, determination of physical and chemical properties of this film; also, its composition. The paper by Shepard is a highly interesting one. He talks about the corrosion of lead and yet he never mentions that surface film that is so highly important. It reminds me very much of a chemist who was supposed to make an analysis of a road-bed. You know how many of our automobile roads are constructed nowadays. There is the thin asphalt surface, and underneath that a layer of concrete, and then your broken stone under that. The chemist takes a drilled sample and he reports so much lime, and so much silica. What do we care about the lime and silica? You would not be able to estimate the life of your automobile tires on that road from that chemist's analysis. You would want to know more about the asphalt "film," its physical properties, thickness,

hardness, etc. First of all, then, there is the question of the composition of the surface film; secondly, the porosity of that film. Practically nothing has been said during the symposium about the porosity. Time and again we have hinted at it, but there are no investigations published, no careful investigations, which deal with the porosity of the film. Thirdly, there is the tenacity of the film, the power of the film to adhere to the underlying metal and of the film to hold together without cracking or peeling. The film may be plastic like rubber, or it may be discontinuous as though it were composed of so many grains of sand; the elastic and the discontinuous film may be of identical composition, and yet entirely different in their protective action. Then, fourthly, there is the micro-structure of the metal, and of the surface of that metal directly underneath the surface film. We need more papers along this line. We need also papers on the mechanical and chemical treatment of metal alloys and the effect of such treatment on the surface film and underlying metal, *i. e.,* the metal d i r e c t l y underneath the film. A clear illustration of this point: a link of the Newburyport bridge was rolled out into sheets and then we were told that these sheets would not stand up as well as the links have stood up for so many years. And why? Because you have produced an entirely different film! Simply because the metal is the same as that of the links, does not prove that the resistance to corrosion will be the same. We also need a better classification of the corrosion phenomena. We ought to define the limits, we ought to be more specific when we talk about atmospheric corrosion, whether we are talking about an atmosphere free from acid fumes or an atmosphere which is practically dry all the year around. Then, when we talk about immersion tests, we want to be pretty careful in defining what acids and what strengths and what temperatures we used. Now, finally, we ought to decide upon a standard measure of corrosion. We have one gentleman who reports in ounces per square foot and forgets all about the time element. Another, reports loss in grams per square foot, which is a bad combination of French and English systems. We must decide upon one uniform measure of corrosion, and the one I would like to propose and have mentioned

before, is the milligram per square centimeter per year unit. If that isn't considered satisfactory let us determine upon some other so that when we record our results let us do so in the same conventional standard in order that we may readily compile and compare results.

W. D. RICHARDSON[7]: May I ask, in order to add a bit of clarity to this compilation, if, in the term "surface film," he intends to include the film or absence of the film concerned in passivity?

COLIN G. FINK: Yes, indeed. Take the case of aluminum metal; we know so little about its film. Dr. Bancroft refers to a case of amalgamation and how the metal all goes to pieces; he knows that the thing does occur, but he does not know w h y it occurs.

E. A. RICHARDSON[8] (*Communicated*): While Dr. Watts' conclusion that "to increase the resistance to corrosion of any metal there should be alloyed with it another metal which is more resistant to corrosion and which forms a solid solution with the metal whose resistance to corrosion it is desired to enhance," may be true in many cases, yet in general the problem of corrosion resistance is not so easily solved as the above statement might infer.

For instance, the following examples are contrary to Dr. Watts' conclusion: Silicon forms a solid solution with iron and is also more resistant to atmospheric corrosion, yet when alloyed with commercially pure iron, at least up to 4.5 percent, materially decreases its resistance to atmospheric corrosion. The same is true of arsenic and tin when alloyed with commercially pure iron and exposed to atmospheric corrosion.

It is interesting to note that the three elements named above all increase the grain size of iron, yet Dr. Watts' conclusion makes no mention of grain size. While his conclusion applies in a general way to corrosion problems, it does not apply rigidly to all cases.

D. M. STRICKLAND (*Communicated*): Mr. Watts has presented in this paper many thoughts which should be considered

[7] Chief Chemist, Swift & Co., Chicago, Ill.
[8] Chemist, National Lamp Works of General Electric Co., Cleveland, Ohio.

when preparing corrosion-resisting alloys. Certain of his conclusions, however, are open to question. I take exception to his theory that increased corrosion resistance properties are added to a metal when alloyed in solid solution with a more resistant metal. He uses as proof for this assertion, results obtained when copper steel is immersed in normal sulphuric acid. This conclusion does not hold true for all types of metals and for all conditions of corrosion. Experiments in which we also used copper steel fail to verify this conclusion. For example, use another acid reaction. Metallic copper is almost insoluble in concentrated hydrochloric acid. One would assume from Mr. Watts' statement that iron, which we find to dissolve seven times as rapidly as metallic copper, would be more resistant if alloyed with copper. Dr. Cushman[9] has shown that this is not the case. We have conducted experiments using concentrated (38 percent) hydrochloric acid, in which copper iron containing 0.20 percent copper lost five times as much weight as pure iron, while copper steel lost ten times more than pure iron.

We have conducted experiments which show that the weight loss of copper iron is eight times the weight loss of pure iron when test pieces are subjected to the action of concentrated nitric acid. Metallic copper dissolves in this acid very rapidly, a 26-gauge sheet 2 x 3 inches dissolves in 2 minutes.

Metallic copper is but slightly attacked when immersed in a solution of aluminum sulphate. According to the author, copper steel should be more resistant under such test conditions than pure iron. Such is not the case. We have repeatedly obtained results which conclusively establish the marked resistivity of pure iron over copper iron, and copper steel when immersed in aluminum sulphate solutions.

Metallic copper loses 50 to 100 times as much weight as iron when both are subjected to the action of concentrated ammonia. Perhaps Mr. Watts believes that in this instance, since copper is the less resistant, the more pure iron you add to the copper the more resistant it becomes, and as the iron content increases and the copper decreases you approach a more and more resistant

[9] Anomalies Encountered in a Study of Immersion Tests of Iron and Steel. A. S. Cushman and G. W. Coggeshall, Am. Electrochem. Soc., 1921, 39, 81.

alloy. We are able to substantiate such a belief, as our experiments have shown that copper steel and irons lost 3 to 4 times as much weight as pure iron when test pieces were subjected to such alkaline condition.

Mr. Watts bases his claim on a single experiment, and only supports his assertion by the results obtained on the action of copper steel when immersed in sulphuric acid. I have shown that his chosen alloy, copper steel, does not in all instances yield corrosion results which verify his own conclusion. The author presents no constructive experimental data concerning the corrosion resistance of aluminum steel alloys, nickel steel alloys, or chromium steel alloys. Since conflicting and contradictory results are obtained using copper steel, no doubt it will be found that other alloys do not conform to the author's theory.

Obviously, Mr. Watts' conclusion is too broad and is not adequately supported by investigational data.

O. P. Watts (*Communicated*): As indicated by its title, the paper under discussion is an attempt to state general principles to serve as a guide in the selection of elements to be alloyed with a given metal for the purpose of producing a corrosion-resisting alloy. The principles stated are based, not on the author's own experiments, but on a consideration of the constitution of the more important corrosion-resisting alloys now in use. The author's view of the importance of the solid solution in alloying to resist corrosion originated several years ago in the attempt to find for his own satisfaction an explanation of the resistance to corrosion imparted to iron by the addition of copper or nickel, electro-negative metals which might, therefore, be expected to accelerate rather than retard corrosion. At that time the number of resistant alloys which were known to be solid solutions were too few to justify the presentation of this view to the public. Even now its acceptance is perhaps a matter of faith rather than evidence, but the writer believes that there are just as exact and definite principles underlying the composition and constitution of alloys resistant to corrosion as hold in any other field of chemical action, and for want of anything better the above views are presented as a working hypothesis.

The photograph concerning which Mr. Rawdon inquires is of

a sample of stainless steel received from the American Stainless Steel Co., and was said to contain about 13 percent of chromium and 0.3 percent of carbon. No mention was made of nickel, and the writer has made no analysis of it. If it were a nickel instead of a chromium steel it would have to contain 50 percent or more of nickel to have withstood a certain corrosion test to which this sample was subjected.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 22, 1921, President Landis in the Chair.

PHENOMENA OF ARC WELDING.[1]

By O. H. Eschholz.[2]

Abstract.

A detailed discussion of metal deposition, fusion and arc stability during electric welding. Under the first item, there are discussed the function of transport of metal by molecular forces, effect of evolution of gases, and vaporization or condensation, with the conclusion that the molecular forces play the main part. Under fusion are considered the effects of impact of ions, atmospheric convection currents, sudden liberation of gases, and combination of material with oxygen and nitrogen. Arc stability is discussed from the standpoints of long and short arcs, constant potential circuits, use of ballast resistance, etc.—[J. W. R.]

Metallic electrode arc welding consists in uniting the members of a joint by an intermediate casting. This casting is formed by drawing an arc from the joint sections, usually a plate, with a wire or rod functioning as the cathode, the latter having such a low thermal capacity that it rapidly liquifies, droplets of molten metal leaving it to impinge upon the fluid metallic surface produced by the anode terminal. This process inherently facilitates securing fusion between the plate surface and the deposited metal—the first requisite of any welding system.

The phenomena of major interest are those causing:

1. Metal Deposition.
2. Fusion.
3. Arc Stability.

[1] Manuscript received February 4, 1921.

[2] Research Engineer, Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.

MECHANISM OF METAL DEPOSITION.

Either the alternating or direct current arc may be employed to secure deposition and fusion. Most commercial systems are the latter, in view of the greater difficulty of stabilizing the alternating-current arc. As this process has, at present, its greatest field in the welding of low, mild, and medium carbon steels, the welding wire employed has a similar carbon content. However, the performance of such wires of the same chemical analysis differs greatly, the variations being introduced by the process of manufacture. Since the anode temperature of an iron arc is greater than that of the cathode and as the thermal capacity of the material to be welded is usually greater than that of the bare deposition wire, the joint material is made the positive terminal of the arc.

A satisfactory deposition rate, consistent with thorough fusion, is achieved by employing a cathode current density in the neighborhood of 8,000 amperes per square inch (1,280 per sq. cm.).

The mechanism of metal deposition under this condition has been the subject of considerable discussion. Prof. R. G. Hudson[3] suggests that "the metal deposited during metallic arc welding is transmitted in part at least in the form of minute particles which are projected from the electrode globule by the internal expansion of some gas, possibly carbon monoxide." Prof. A. W. Slocum[4] advances the hypothesis that most of the metal is transferred in the form of vapor. Careful examination of the performance of a variety of bare electrode wires has led the author[5] to conclude that metal transfer may be accomplished in part by:

1. Vaporization and condensation of electrode material.
2. Expulsion of vaporized and liquified metal by the expansion of gases confined or generated in the electrode ends.
3. Transport of liquified metal due to the forces of molecular attraction, gravity, surface tension, adhesion, cohesion.

While all three of these means are available for the deposition of metal, it is the author's conclusion that under good welding conditions at least 85 percent of the deposited metal is transmitted in liquid form through the action of molecular forces.

[3] Journal American Welding Society, Vol. I.
[4] Welding Engineer, Jan., 1921, p. 23.
[5] Elec. World, June 26, 1920, p. 1473.

PROPORTION OF ELECTRODE VAPORIZED.

The importance of this factor may be evaluated by determining the rate at which the filler or wire electrode metal is consumed and comparing the energy absorbed at the bare wire negative electrode terminal with that obtained by calculating the energy necessary to vaporize an equivalent amount of metal.

It has been found by test on welding with an 18-volt, 150-amp., arc that a mild steel electrode, 5/32 in. (3.9 mm.) in diameter, is consumed at the rate of 3.1 lb. (1.4 kg.) per hour. The distribution of arc voltage is estimated to be as follows: Anode drop, 9 volts; cathode drop, 7 volts; arc-stream drop, 2 volts.

The energy input at the negative arc terminal is, therefore, of the order of 1,200,000 watt-seconds per pound of electrode metal. The energy required just to vaporize one pound of iron is of the order of 3,100,000 watt-seconds, assuming a boiling point of 2,450° C. a latent heat of fusion of 1,120 therm-grams and a specific heat of liquid iron of 0.20. It is at once evident that under normal welding conditions only a small proportion of the electrode metal may be vaporized. Overhead welding tests in which the choice of electrodes and arc length were such as practically to eliminate metal transfer due to gas expansion or molecular attraction, indicated the amount of metal deposited by condensation to be of the order of 5 percent. A reasonable estimate of the distribution of negative-arc-terminal energy on welding downward appears to be as follows:

	Watt-Secs.	Energy Percent
Liquefaction (2,000° C.) of 90 percent of wire electrode.	720,000	60
Vaporization (2,450° C.) of 10 percent of wire electrode.	310,000	26
Radiation, conduction, convection losses.....	170,000	14
Approximate energy per pound of wire electrode consumed	1,200,000	100

EXPULSION OF METAL.

This effect is present to some degree in all commercial welding wires. It is well known that metals absorb gases readily, the quantity varying greatly with their characteristics, preparation and exposure. Iron has been found to contain under some conditions fifty times its volume of gas. Upon striking an arc with electrodes

high in occluded gas the pressure obtained by the rapid expansion of the confined atmosphere exerts a propulsive force on the inclosing fluid metal, scattering it approximately radially from the electrode end. This may be confirmed by dipping a welding rod in an acid (H_2SO_4, HCl, etc.) for a few minutes to permit the occlusion of hydrogen and then striking an arc. An increase in the volume and agitation of arc gases, as well as scattering of metal, may be observed at once. This performance characterizes an abnormal electrode. Tests made with electrodes high in various occluded gases have failed to indicate an increased deposition rate due to the functioning of the gaseous blasts. Moreover, the emission of such blasts distinctly serves to de-stabilize the arc stream and thereby prevents the maintenance of a short arc length, particularly essential for overhead welding.

Some electrode wires contain relatively large quantities of included iron oxide and slag. Upon heating the electrode end such impurities disintegrate and liberate oxygen, which then combines with the carbon present to form carbon monoxide and carbon dioxide. The expansion of these generated gases tends also to propel the fluid metal across the arc stream. However, again no increased deposition rate was evident during test, owing to metal transferred in pellet form. It is characteristic of low-carbon steels that the metal becomes permeable over a critical-temperature range. This condition permits the influx of oxygen with the resultant generation and expansion of gases in the interior of the electrode terminal. This effect is obtainable, apparently, to an appreciable degree only upon welding with a long arc.

Expansion of occluded or generated gases occurs to only a slight degree when holding a short arc length with wires that comply with the specification drawn by the American Welding Society. The effect obtained is not explosive in action, but may be described as a slow enlargement of the globular-electrode terminal. Expansive forces of this order appear to aid metal deposition by decreasing the forces of cohesion and surface tension retaining the globule on the end of the wire electrode. If the arc is interrupted in a neutral atmosphere the globular electrode tip may be observed to decrease in size, owing to the diffusion of confined gases and shrinking of the liquid metal.

When the use of welding wires high in occluded or generated gases is unavoidable, the arc should be stabilized by coating the electrode with a flux and increasing the circuit voltage or reactance. Metal plates, shapes, etc., are also found occasionally with a high gas content, particularly if they have been preheated in a gas furnace. This condition may be recognized by a vicious, snapping, sputtering arc, frequent arc interruption and tendency for the arc stream to move rapidly from the initial point of electrode contact. Welding conditions may be improved by the use of a very short arc, blocks of copper or like material on both sides of the zone to be welded, flux-covered electrodes, and increased circuit voltage or reactance.

MOLECULAR FORCES CAUSING DEPOSITION.

Most of the pencil-electrode metal appears to be transported and deposited in globular, liquid form, upon either welding downward or overhead when the electrode-current density is of the order of 8,000 amp. per square inch (1,200 amp. per sq. cm.). The metal transfer appears to be accomplished by:

A. Downward Welding.

(1) Long Arc: Formation and growth of a liquid globule at electrode terminal until its weight, or gravitational force, exceeds the sum of the forces of surface tension and cohesion, tending to retain the globule at the electrode.

(2) Short Arc: Growth of globular end until contact is made with a wetted surface (plate metal liquefied by anode energy), the forces of adhesion and surface tension at the plate surface then assisting the gravitational force in drawing the globule to the plate.

B. Overhead Welding.

(1) Long Arc: Slight deposition due only to condensation of vaporized metal or pellet impact.

(2) Short Arc: Globular growth until contact is made with liquefied plate or deposit surface, whereupon the forces of adhesion and surface tension at the plate overcome the combined forces of gravitation, cohesion and surface tension acting to hold the globule to the electrode surface.

CHARACTERISTICS OF DIFFERENT ELECTRODE MATERIALS.

Globular formation at electrode terminal is characteristic of bare, coated, and covered wires. The size, appearance and homogeneity of such globules vary greatly with wire analysis, diameter, covering, polarity, current density, arc length, impurities, and perhaps mechanical working and heat treatment. Bare electrodes that have been examined by the author may be classified in four groups.

Group 1: The globular formation is most evident upon welding with drill rod. As this steel is made by the crucible process, it is low in impurities and gas content. Sections through the globule show, therefore, solid metal even after holding a long arc. The high carbon content (1.2 to 1.4 percent) serves to generate a thick envelope of carbon-oxide gases which greatly reduces the further oxidation of the electrode surface, maintaining it in the approximate form visible during the welding. Such globules may be readily obtained upon drawing an arc with a drill rod ⅛ in. (3.2 mm.) in diameter, using a welding current of 100 amp. and lengthening the arc stream as the globule increases in size. When a long arc, 3/16 in. (4.7 mm.), is held, the electrode end enlarges until a characteristic maximum diameter is secured. At this diameter the weight of the globule equals the attractive forces holding it to the electrode, so that further enlargement causes the liquefied metal to fall from the electrode end, dropping to the plate in downward welding, or flowing down the electrode in overhead welding. On holding a short arc length the growth is limited by contact with the plate surface, when the forces of surface tension and adhesion assist in metal transfer.

Fig. 1 shows drill-rod globules. The particular characteristics are regular contour, slight oxidation and solid section. In Fig. 5a* are shown both the arc stream and globular end; in Fig. 5b the globular end has been released, while in Fig. 5c globules are shown deposited on the plate with one forming at the electrode terminal. Fig. 5f shows the contour of the globule immediately after interrupting the arc, the exothermic reaction of atmospheric oxygen and surface carbon developing sufficient radiant energy to permit

* Photographs taken with Multi-Exposure High Speed Camera described by Mr. J. Legg in Dec., 1919, Elec. Journal.

photographing the terminal. A slight irregularity in contour due to such oxidation may be noted.

Group 2: Mild carbon steel is frequently employed as welding wire. Upon forming a globular end and breaking the arc, atmospheric oxygen rapidly attacks the unprotected incandescent iron, often leaving only a perforated iron oxide shell. In Fig. 2a are shown typical exhibits of such oxidized globular ends. During welding, however, the metal is exposed to a much slower rate of oxidation, due to the protection offered by the inclosing gases. To obtain a true exhibit of globule conditions during welding, it is necessary to cool the electrode, after interrupting the arc, in an inert atmosphere. The characteristic formation then obtained is shown in Fig. 2b. The solid section and contour now resemble those secured with drill-rod electrodes. This formation may be obtained by holding an arc from the bottom of a hole 2 in. (5.1 cm.) deep, ¾ in. (1.9 cm.) in diameter, and interrupting the welding current when the electrode is surrounded by dense arc fumes. Fig. 5d shows the small globular electrode end on welding with a short arc, while Fig. 5e shows the electrode end shortly after the release of the globule.

Group 3: The presence of occluded or generated gases is practically unavoidable in steels and iron made by the Bessemer and puddling processes. The expansion of such gases in the liquefied electrode end produces characteristic cavities in the wires examined. These cavities occurred singly or in groups, varying widely in size and distribution. Deposit tests indicated that the cavitous condition could be readily obtained in the transferred metal. Fig. 3 shows typical electrode and deposit exhibits of this group.

Group 4: Upon breaking a long arc held with a low carbon-content wire electrode, an interesting modification in globular structure may be obtained. It is well known that commercially pure iron passes through a critical temperature range, in the neighborhood of 950° C., in which the metal assumes a more permeable form. This condition obviously facilitates the penetration of atmospheric gases and therefore the formation and expansion within the fluid globular body of carbon oxide gases. This expansion causes the globule to enlarge in the typical hollow forms shown in Fig. 4. Mild steel electrodes also possess this

characteristic although to a less degree, as is shown in Fig. 2c. In the latter exhibit a distinct line of demarcation is visible between the globular shell and solid electrode, where, presumably, the critical temperature zone existed, facilitating oxygen penetration.

The structures shown in Figs. 2c and 4 are, to the author's knowledge, characteristic only of long arc welding and should not therefore occur while following correct welding procedure. This is substantiated by the fact that welds made with either Group 2 or Group 4 electrodes are comparatively free from perceptible gas pockets.

In Figs. 5a, b, c is given a photographic record of the sequence of metal deposition phenomena under the exaggerated conditions encountered on employing a high carbon-content steel wire. In Figs. 5d and e the sequence of phenomena is shown when using the usual low carbon-content rod. The cycle of deposition appears to be as follows:

1. After forming the arc, appreciable time is required to liquefy the electrode end.
2. The liquefied end assumes a globular form, enlarges, decreasing arc length and arc voltage, while increasing arc current.
3. When the globule has enlarged sufficiently to bridge or short-circuit the arc stream, the arc voltage drops to practically zero and the arc current increases to short-circuit value.
4. The short-circuit condition exists until the globule is no longer in contact with the wire electrode.
5. At the instant of detachment the current decreases while the voltage rises sufficiently to re-establish the flow of the welding current in the partially de-ionized arc gases.

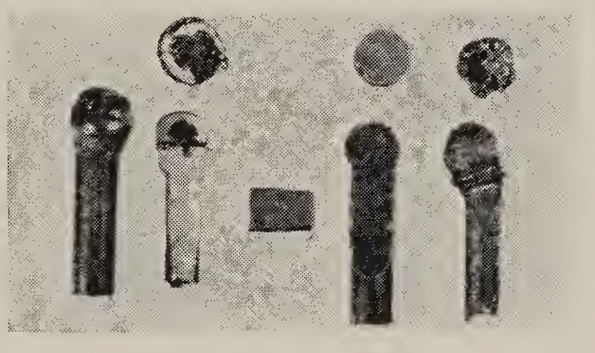
Fig. 6 shows this cycle graphically. Fig. 7 illustrates circuit characteristics upon holding a short arc with a mild-steel electrode. The high rate of globule transfer is clearly evident by the frequency of current peaks at the instant the arc stream is short-circuited by the deposited globule.

OVERHEAD WELDING[6]

Overhead deposition is chiefly dependent upon arc phenomena overcoming gravitational force acting on the material of the

[6] See Discussion of "Overhead Welds," O. H. Eschholz, Power, Nov. 16, 1920.

Fig. 1. Surface and section views of globular electrode tips and deposited metal on welding with a ⅛″ diameter drill rod. Note absence of cavities.



a b c

Fig. 2. Results with mild steel rods.
a and c. Oxidized appearance when arc is broken in air to examine tip. Deposited metal at right of a is, however, solid.

b. Section free from cavities when arc is broken in inert or reducing atmosphere, structure resembling that in Fig. 1.

Fig. 3. Cavities formed in globular tip and deposited metal on welding with a Bessemer steel high in occluded gases and impurities.

Fig. 4. Appearance of low-carbon-steel electrodes, oxidizing atmosphere and long arc.

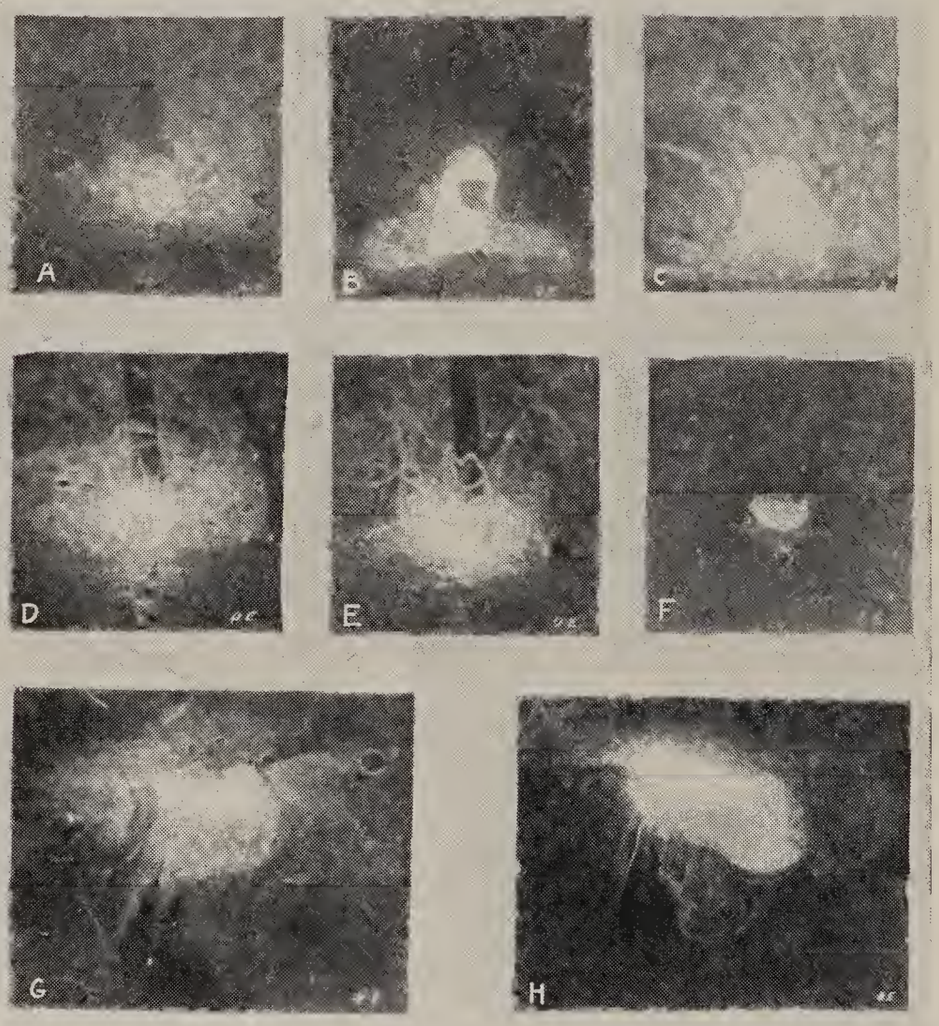


Fig. 5. Appearance of the welding arc:
a, b, c. Sequence of metal deposition on holding a long arc with drill rod. Note the following stages, globular formation, transfer and deposition.
d, e. Downward welding with a mild-carbon-steel electrode showing electrode terminal before and after globule deposition.
f. End of wire electrode terminal, approx. 0.001 sec. after rupturing arc.
g. Overhead welding arc, short-arc length; note globular end and deposited layer.
h. Long overhead arc; note absence of deposited metal and stricted-rod-electrode surface caused by downward flow of metal.

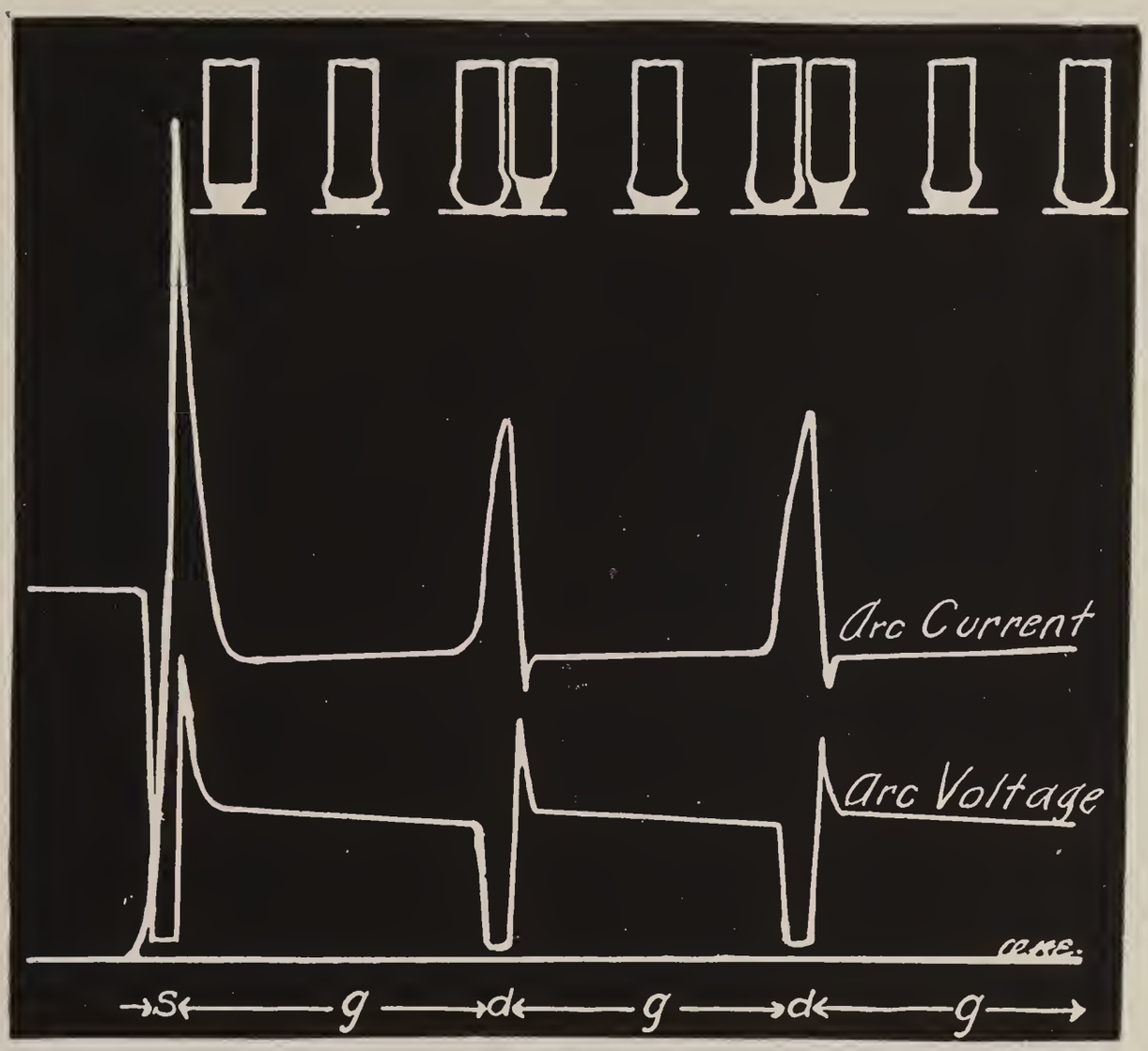


FIG 6. Cycle of metal deposition (downward) and variation of arc current and arc voltage. S, starting of arc; g, growth of liquid globule, d, deposition of globule.

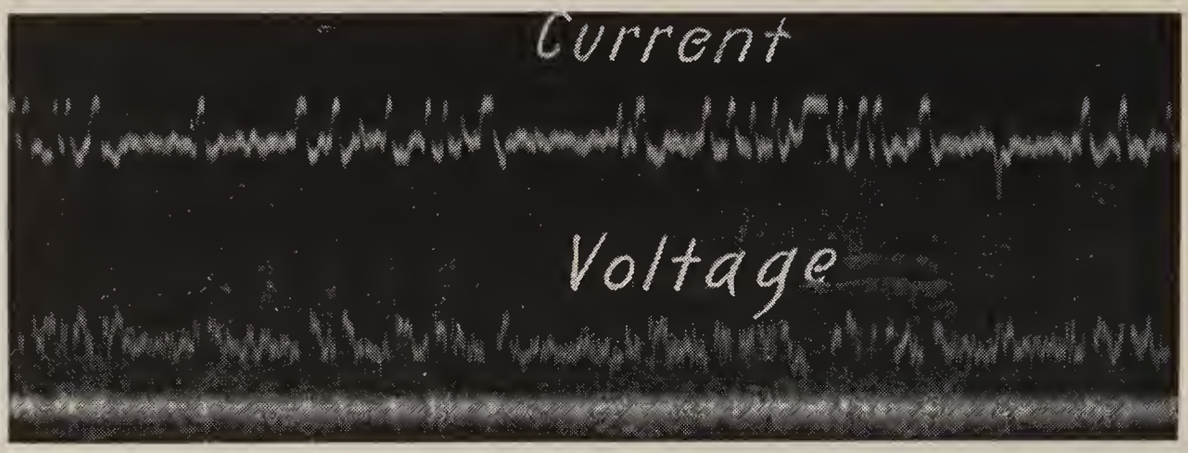


Fig. 7. Oscillograph record of arc current and arc-voltage variation when holding a short 160-ampere arc. Note current peaks indicating instant at which globule short circuits arc, at the rate of about 25 per second.

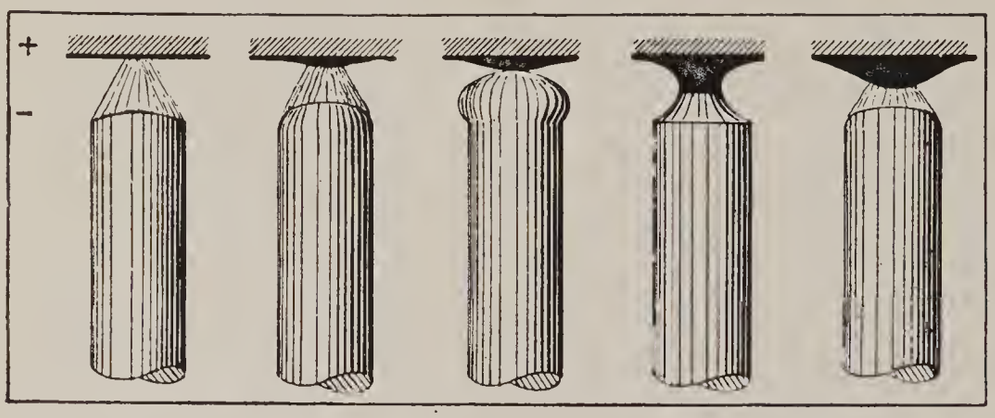


Fig. 8. Cycle of metal transfer on overhead welding.

Fig. 9. Typical crater and deposited layer formed with welding arc.

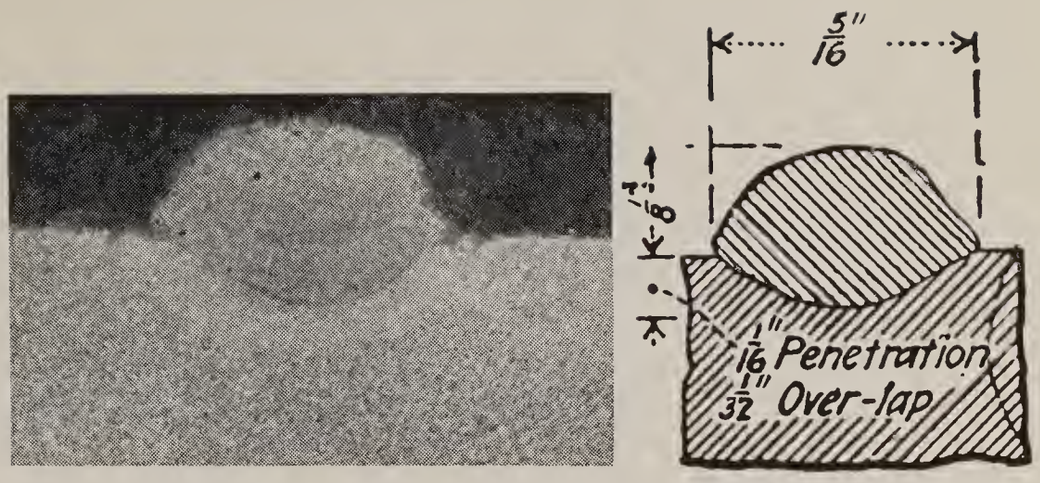


FIG. 10. Etched section through deposited layer showing how transferred metal is fused to crater surface. Note characteristics of penetration overlap and contour of typical and satisfactory deposit.

FIG. 11. Etched cross section through a deposit consisting of a series of built-up layers showing fusion pattern. Note two types of electrodes were employed to facilitate reproducing etched surfaces.

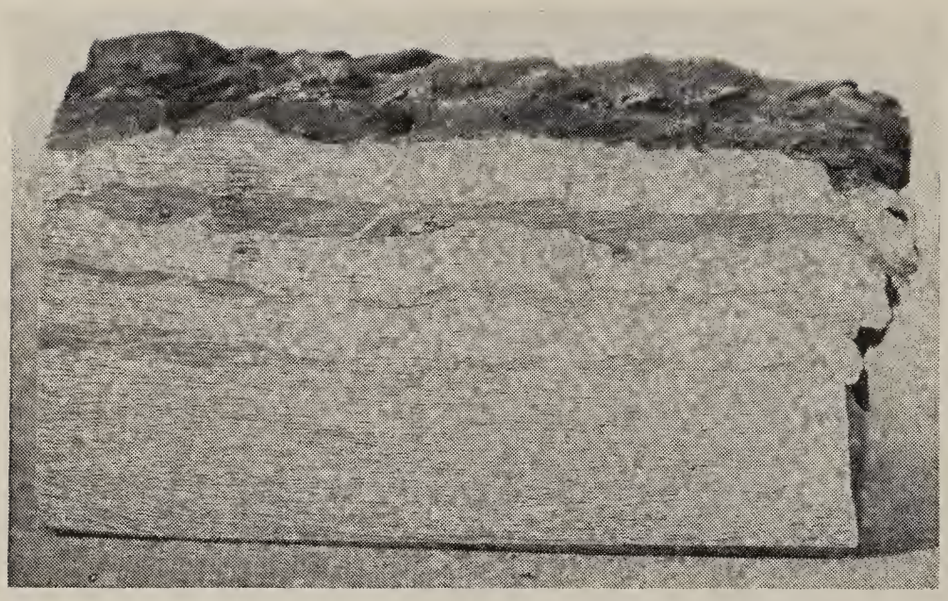


Fig. 12. Longitudinal section through deposit shown in Fig. 11.

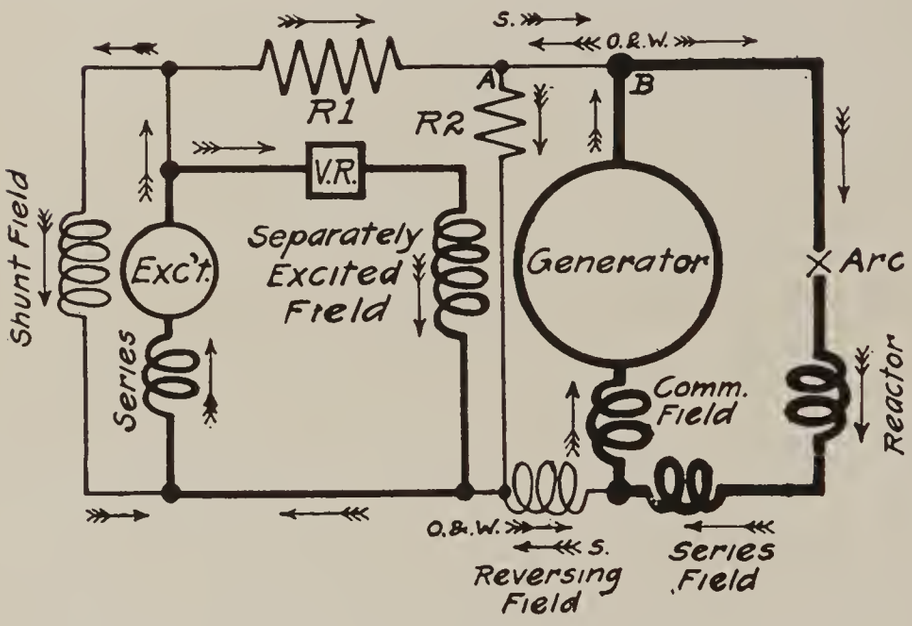


Fig. 13. Wiring diagram of portable, arc-stabilizing generator shown in Fig 14.

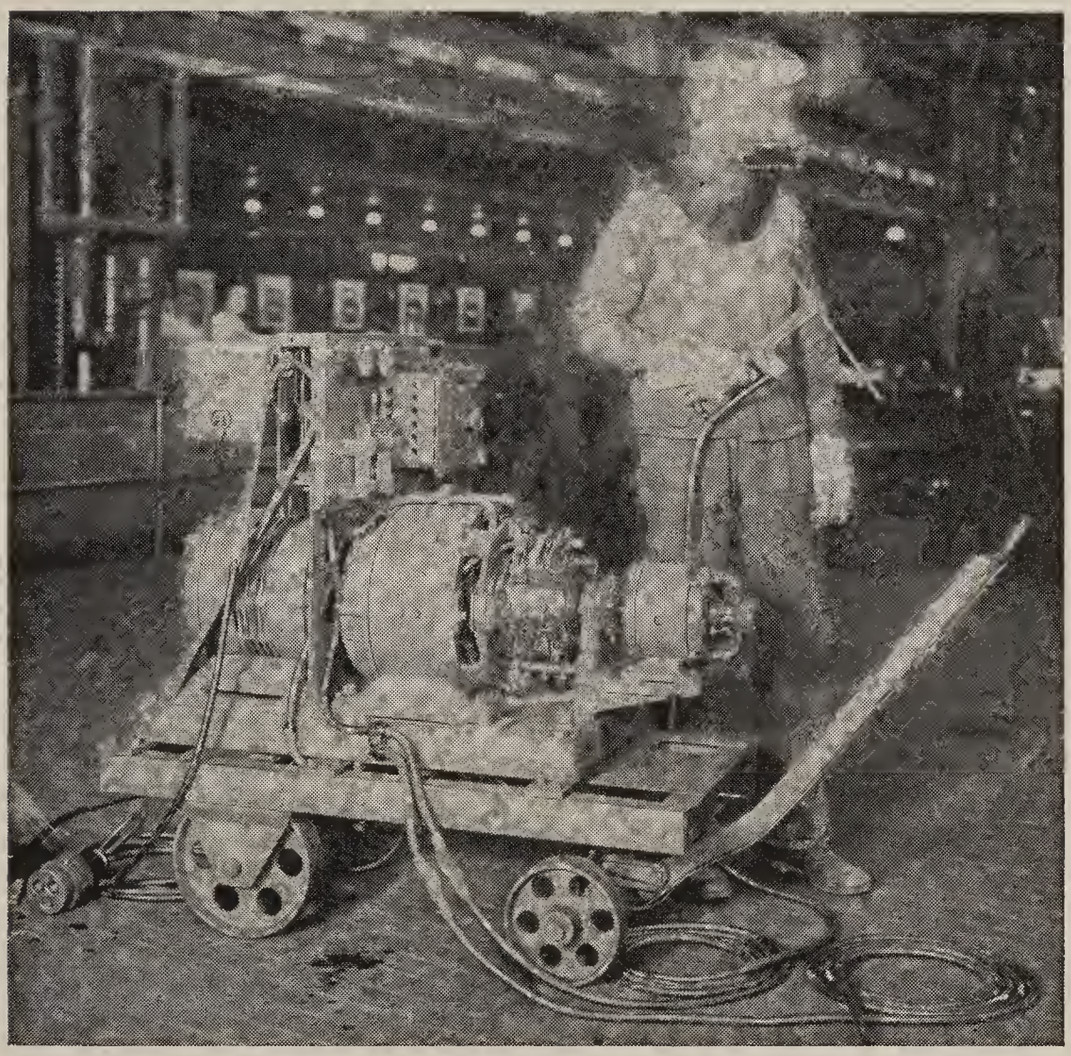


Fig. 14. Single operator portable welding generator and welding equipment.

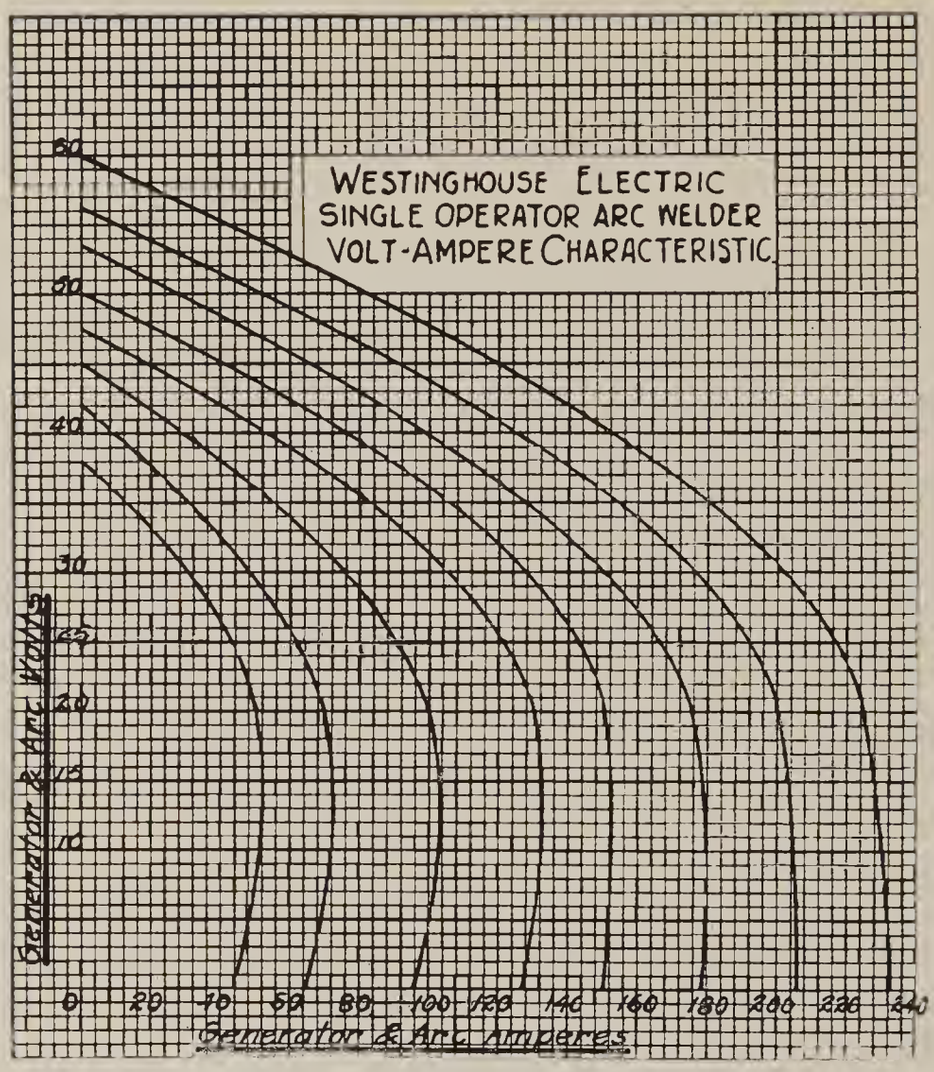


FIG. 15. Volt-Ampere characteristic of generator for various current settings. Note approximate constant current from short-circuit to arc voltage of 25.

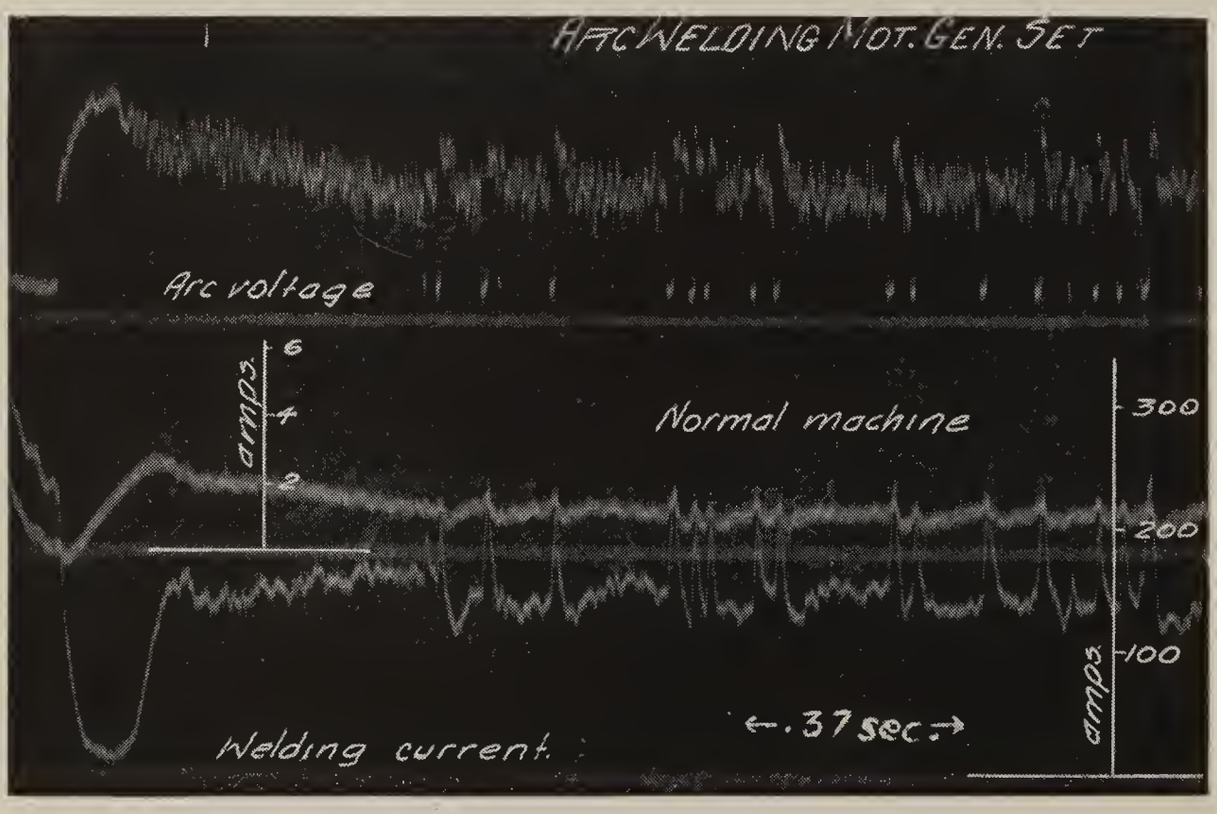


FIG. 16. Oscillograph record of arc voltage, upper, and arc current, lower, variations, showing response of generator during the start and maintenance of a 160-ampere-welding arc.

pencil electrode. The facility with which deposition is accomplished is a function of arc current and arc length, as well as choice of electrode diameter and electrode material. To convey the globule resting on the end of the pencil electrode to the overhead plate the lifting force must exceed the retaining forces of gravity, cohesion and surface tension at the wire perimeter. Obviously the problem of transferring the globule may be simplified by decreasing the forces tending to retain the globule on the electrode end.

By producing only small globules the weight of liquid metal may be held to a low value. As the size varies, within limits, with the arc length, the maintenance of a short arc of from 1/16 in. to 3/32 in. (1.6 mm. to 2.4 mm.) will therefore insure a controllable globule weight. Other factors determining the magnitude of the total retaining force are the unit surface tension, unit cohesion and the contact area between the liquid globule resting on the solid end of the pencil electrode and the electrode.

The surface tension and cohesion between the solid wire and its molten end are decreased by the presence of solid, liquid and gaseous impurities at the boundary. Quantitative information on this subject is not available. Experience, however, has shown that these forces are reduced by the phenomena occurring when small quantities of iron oxide, iron carbide, manganese, etc., and occluded gases are present in the electrode during the deposition process.

The total surface tension and the total cohesive force are proportional to the area of contact between the liquid and solid or plastic metal. It is obvious that these decrease with the diameter of the electrode and also with the total energy developed, and therefore with the arc current. The facility with which the electrode surface becomes "wetted," thereby affecting the contact area, varies with its analysis, melting temperature, physical properties of the surface and the current density. A satisfactory evaluation of the importance of each of these factors has not been made, although it is well known that different types of electrodes employed for downward deposition vary greatly in their "wetting" action and therefore in their characteristic retaining force and ease of overhead deposition.

The lifting force is comparatively a fixed quantity, since the material and thermal characteristics of most overhead joints vary but little. The total lifting force is a function of the surface contour and of the area puddled by the positive crater. It is also dependent upon the "wetting" characteristic which facilitates the adhesion and spread of the electrode globule on making contact with the puddled surface. The rate at which the plate metal absorbs heat energy from the deposited metal determines the rate of congealing of the electrode metal and therefore is a factor in determining the magnitude of the lifting force. Heating an overhead joint locally helps to start layer deposition, since it facilitates the initial production on a cold plate of a "wetted" surface to which the globule must be attached by the forces of surface tension and adhesion. However, if the joint temperature is uniformly increased to a high value, deposition will be retarded, since the rate of congealing of deposited metal is decreased.

The cycle of deposition appears to be as follows:

1. Metal at each terminal is liquefied upon striking an arc.

2. The molten electrode end assumes an approximately spherical form, due to the well-known phenomena of surface tension causing a fluid material to contract into the smallest volume.

3. This globule enlarges with continued application of energy, until with the aid of electrode manipulation its upper surface is brought into contact with the overhead pool, thereby short-circuiting the arc stream and causing the lifting forces to act upon it.

4. Forces of surface tension and adhesion at the contact area between the overhead plate and the globule cause the globule to change its form and spread over the plate surface.

5. As the metal spreads, the area in contact with the plate increases and therefore the lifting forces are also increased, causing an acceleration in metal transfer. These forces act until the globule is lifted off the wire electrode end, when the short circuit is broken and the arc re-established.

This deposition sequence is shown graphically in Fig. 8. The arc voltage and arc current variations are similar to those shown in Fig. 7 for short arc downward deposition. The molecular force phenomena of overhead metal deposition may be simulated by employing a mercury analogy. This consists essentially in trans-

ferring a globule of mercury, resting in the cupped end of a steel rod, to an overhead amalgamated surface. When contact occurs between the globule and amalgamated plate, mercury passes to the overhead surface with such speed that it appears to leap from the rod to the plate, a behavior resembling that occurring in the welding arc.

Although the knowledge concerning the behavior of the welding arc is still incomplete, the hypothesis that metal transport is chiefly caused by the forces of molecular attraction facilitates the interpretation of important arc phenomena and offers as well a basis for the ordered determination of electrode requirements, apparatus design and welding characteristics.

MECHANISM OF FUSION

The crater formation at the anode of a carbon arc drawn in atmospheric gases is a well-known phenomenon. The crater at the anode or plate surface in a welding arc is somewhat similar, and a typical and important characteristic of the process. Immediately after drawing a short arc, the plate metal first liquefied appears to be blown from the crater terminal, which continues to penetrate deeper into the anode material. This displaced metal is thrown to the edge of the crater and cools in ridges. With a proper combination of arc current and cathode current density it is therefore possible to convert the welding arc into a cutting arc. While the source of this blowing action has not been definitely established, the following effects appear to be contributory:

1. Impact of ions, cathode vapor, gases and globules.
2. Atmospheric convection currents.
3. Sudden liberation of gases confined in anode material.
4. Pressure on anode surface of gases formed by combination of incandescent metal constituents with atmospheric gases.

This crater, penetrating the surface of the members to be welded, serves as a repository for the liquefied wire electrode. In Fig. 9 is shown a typical crater while Fig. 10 illustrates the manner in which the "arc metal" is deposited and fused to the anode material. The character of this penetration, fusion boundary, overlap at the edges, and surface contour is significant of arc manipulation, metal properties and welding circuit. A more

complete discussion of these factors is given by the writer in "Fusion in Arc Welding," in the March, 1919, Proceedings of the Am. Inst. Electrical Engineers.

To complete a weld or build up a metal section, such fused "arc metal" is deposited in layers and then in tiers. Figs. 11 and 12 show the fusion patterns between adjacent layers as well as between such layers and the base plate. Arc metal so formed has been found to have an ultimate tensile strength of 58,225 pounds per square inch (40.75 kg. per sq. mm.), elongation of 18 percent and reduction of area of 27.8 percent. A complete discussion of "Properties of Arc Metal and Arc Welds" is given by the author in the Feb. 15, 1921, issue of "Power."

ARC STABILITY.

The necessity of stabilizing arcs drawn on direct-current, constant-potential circuits is generally known, the common method being to connect in series a ballast resistance having a voltage drop usually no less than 50 percent that of the arc. Owing to the great de-ionizing effects the welding arc is exposed to, due to the arc manipulation, convection currents, air drafts, movement of terminals over cold surfaces, etc., a much greater ballast resistance having a voltage drop of the order of twice that of the arc is necessary. Since the mean potential of the welding arc varies with proper manipulation between 18 and 22 volts, the lowest commercial constant-potential circuit that combines economy of energy and space with an arc stabilizing circuit is 60 volts.

The extension of arc welding to a great variety of purposes has created an insistent demand for a compact, portable single-operator generator. To satisfy the requirements of a welding arc such a supply circuit should possess the following characteristics:

1. Ease of arc establishment when electrodes are cold.

2. Freedom from "sticking" or "freezing" of electrodes on short-circuiting arc stream.

3. Maintenance of a short stable arc and approximate constant current value during growth of liquid globule.

4. Increase of welding current at the instant, and during the period in which the globule short-circuits the arc stream. This is essential if adequate penetration is to be secured in short-arc

welding, the increased I^2R energy replacing to a considerable extent the arc-terminal energy lost on short-circuiting the arc stream.

5. Rapid increase in arc voltage at instant of globule detachment, for the purpose of facilitating the re-establishment of a stable arc.

The usual type of constant current generators employing separate field excitation is too sluggish in its reactions to meet the above requirements. If a large inductance is connected in series, difficulty will be encountered in securing adequate penetration; furthermore, owing to the ease of holding a long arc, oxidation of the metal during transfer is facilitated. To satisfy the above requirements it has been found necessary to embody in the generator the circuit shown in Fig. 13. The 175-ampere single-operator unit[7] shown in Fig. 14 supplies the desired welding-circuit characteristics; Figs. 15 and 16 show a similar system with a satisfactory degree of portability and efficiency, the complete unit occupying less space with about half the weight and double the electrical efficiency of the single-operator constant potential unit which it displaces.

In the past, investigators of arc phenomena have confined their attention chiefly to the behavior of low-current arcs. The problems, however, confronting the welding, searchlight, fuse and circuit-breaker engineer can only be solved with a proper knowledge of high-current arc phenomena. While certain fundamental characteristics are common to both types of arcs, it is evident that the complexity of the phenomena may increase with increase in current, rendering more difficult their proper interpretation and retarding their most effective utilization.

DISCUSSION.

J. A. Seede[1]: There are several factors that have an important bearing on successful arc welding, and if we consider them in the order of their importance, I think all will agree that the operator's

[7] The characteristics of this unit are discussed more fully in the following articles: A. M. Candy, Proc. A. I. Elec. Eng., June, 1920; O. H. Eschholz, Elec. World, July 17, 1920.

[1] Electrical Engineer, General Electric Co., Schenectady, N. Y.

part is the most important. Unless the arc is stable, the weld will not be successful, and it certainly requires a good operator to hold a stable arc. As Mr. Eschholz has pointed out, a good operator, with a good electrical circuit and comparatively poor electrodes, can make a fair weld, but a poor operator, even with the best electrodes and the best electrical circuit, can hardly hope to make a good weld. It is obvious that an equipment that will eliminate the most important factor, especially when it is a variable factor, should have a profound effect on the future of arc welding, and I am calling the attention of the meeting to the fact that there is now available an automatic arc welder that eliminates the human element and practically insures the perfection of every arc weld.

James Kelleher[2]: I should like to ask Mr. Eschholz if, in the study of arc welding arcs, he has come across the phenomenon described last autumn, of the double arc, that is, an arc emanating from the work and at the same time coming from the electrode? In this case I am speaking of graphite electrodes, welding onto a plate. That is where one arc apparently comes from the electrode and one arc comes from the work to be welded.

O. H. Eschholz: In reply to Mr. Kelleher's remarks, I wish to state that I have not observed what may be conveniently termed the dual arc stream phenomenon in metallic electrode arc welding. However, upon drawing a direct current arc between graphite electrodes, in a weak magnetic blowout field, two distinct arc streams, one issuing from each terminal, may be readily observed.

James Kelleher: I have asked the question because I have observed this dual arc phenomenon in direct currents, and within the last two months we have taken on a motion picture about 150 feet of film on this phenomenon. The furnace was of the Siemens type. The electrode was a 3-inch graphite electrode, and the bath, as a bath contained nickel, and the arc then was apparently 4 inches in length and the dual arc extended in some cases to a length of between 6 and 8 inches to one side of the arc, and in

[2] Asst. Eng., Goderich, Ont., Canada.

many cases caused rupture of the arc and caused the furnace to slow down considerably.

C. J. HOLSLAG[3]: The question of how the metal passes from the electrode to the work has been undecided for the last twelve years, and it is further from solution now than, say, ten years ago, when all agreed that the magnetism carried or pushed the metal across; electrode holders were made with turns of wire, both series and shunt, in order to successfully do overhead welding. I remember distinctly making a huge hollow coil to magnetize a locomotive crown sheet so as to permit overhead weld. The only result obtained was the verification of the well-known magnetic blow-out action on the arc. I do not believe that the metal goes across in globules when welding successfully. Globules do cross the arc, however, when the arc is too long, when electrode-current density is too high, when too many B. T. U.'s are liberated per minute, when the electrode melting point is much lower than the plate, and in some other more rare cases; but when a good, close arc is held, say with an automatic holding arrangement, there are no globules, large or small. It is certain that the temperature of the filling electrode and the temperature of the work electrode are that of molten iron, and this molten iron disengages from the solid part of the filler rod to re-combine with the solid part of the work electrode.

In my opinion it is certainly wrong to consider the drop and the current at either electrode separate from the arc stream. The problem could be put simpler by considering that there are so many watts, which is the total volts drop multiplied by the current through the arc, and which rate of heat energy determines the melting of both the electrode and the plate. I agree with Mr. Eschholz that there are not enough total watts to completely gasify the amount of metal deposited so that the metal must go across either in particles or as a vapor, and as I personally have never been able to see the particles, I believe it to be a vapor, which condenses on the work electrode. Mr. Eschholz has described the process of overhead welding perfectly. The action is simple. One drop of water will hang to a ceiling; but when two

[3] Managing Engr., Electric Arc Cutting & Welding Co., Newark, N. J.

drops collect at one point, one falls. The process of overhead arc welding consists of moving along to a colder place and having the first drop freeze behind before the second drop falls.

It is not so long ago that overhead welding was only thought possible with direct-current electrode negative; but welding with alternating current has somewhat disrupted this as well as several other D. C. pet theories. One of these theories that has not disappeared entirely as yet is that in direct-current welding with the electrode negative, 60 percent. of the heat is in the work. To be sure, with two equal electrodes, as in arc lighting, such is the case, but the simple fact has been overlooked that with the electrodes of unequal size, say a 2-inch carbon electrode and a 1-inch carbon electrode, there is greater heat in the 2-inch electrode, regardless of its polarity. In the case of arc welding, the disparity in the size of electrodes is a thousand times more marked. The general case is the 5/32-inch electrode welding to a plate or mass of metal many hundred times greater. In this case there is greater heat in the work electrode, irrespective of polarity, as with alternating current where polarity troubles are forgotten.

Besides these theoretical arguments, there is the obvious practical result that the heat in the electrode at any instant is transferred to the work at the next instant. For example, you cannot draw an arc but what some metal will be deposited, so that the molten metal of the crater of the work consists of some of its own metal molten with more of the electrode metal deposited, which deposition carries all the heat that was, the previous instant, in the filling-electrode.

There is a difference, however, between direct current with reverse polarity and a difference between these two and welding with alternating current. This phenomenon is a difference in rate of melting of the filler material; *i. e.,* the electrode. The speeds of deposition are approximately as follows: Taking the negative electrode as one, the A. C. as two, and the D. C. positive as three. Except for the most crude filling or padding, D. C. with the electrode positive is too rapid to be controlled, by the human hand. There has been no type of welding yet developed where the speed of A. C. cannot be taken advantage of by the operator, and in general, increased speed, providing equally good results are obtained, is a great asset.

As to the question of results, I would point to the test made by the Bureau of Standards at Washington, D. C., during the war, where about twenty D. C. systems were exemplified and only one alternating arc, and in which the only specimens which were stronger than the plate under tensile test were those made by alternating current, and this at no loss of good results under the other tests, "cold bend" and "alternating stress."

O. H. Eschholz: I am in agreement with Mr. Holslag on some phases of the alternating current arc, but at the present time this arc, for welding purposes, has certain limitation, and to narrow the scope of the discussion I have treated only direct current arc phenomena. Mr. Holslag concedes globular deposition on welding with a long arc, but assumes a continuous steam of molten metal flowing between terminals upon shortening the arc. In this connection the discontinuity in arc voltage and variation in arc current shown in Figs. 6, 7 and 16 should prove instructive, as they clearly indicate intermittent metal deposition even with a short arc length.

Henry Hess[4]: A dual arc has been spoken of, and I understand that to mean that successive arcs emanate first from one and then from a second electrode. If that is based on theoretical conclusions, I have no quarrel. But apparently it is based on observation, and observations made by the camera. I understand that the speed of an arc is far beyond the speed of the taking of any successive pictures. I think that standard successive motion picture camera machines do take sixteen per second as the standard rate, but the speed of an arc is far beyond any such possibility, and I would be very much interested in the consideration of a camera that would operate at such speed as to show the successive stages of such arc, and I doubt that such pictures have ever been taken.

O. H. Eschholz: With reference to Mr. Hess' remarks, I wish to state that while no exhaustive examination has been made of this "dual arc" phenomenon, nevertheless under favorable conditions the separate streams are clearly evident, and appear quite stationary, issuing from each electrode and resemble some arc phenomena encountered in vacuo.

[4] Philadelphia, Pa.

A. W. Slocum[5] (*Communicated*): In this paper, Mr. Eschholz has added a valuable contribution to the science of welding. He has rendered special service in emphasizing the role of surface tension and its related "adhesion" and "cohesion" phenomena. In one respect I would extend the role of this action still further than Mr. Eschholz does in his paper.

It plays the chief role in the production of the crater and the ribbed appearance of the weld. This is pertinent to a discussion of the paper, as Mr. Eschholz ascribes the formation of the crater to a kind of blowing action. He says: "While the source of this blowing action has not been definitely established, the following effects appear to be contributory: 1. Impact of ions, cathode vapor, gases and globules. 2. Atmospheric convection currents. 3. Sudden liberation of gases confined in anode material. 4. Pressure on anode surface of gases formed by combination of incandescent metal constituents with atmospheric gases."

The excess of "blowing action" above that of the enumerated causes is due to the fact that the surface tension is decreased by rise of temperature. Were it not for this temperature effect, the metal would not be lifted by the surface tension from the electrode to the plate against gravity, as Mr. Eschholz suggests in overhead welding.

In forming the crater the surface tension at the cooler edge of the hot spot is stronger and pulls the surface metal from the center outward toward the edge, and the irregularity of the cooling action at the edge is the chief factor in producing the ribbed appearance of the weld.

When a molten globule falls from the electrode to the plate a similar action occurs. The top of the globule exposed to the heating action of the arc has its surface tension weakened, and when the surface of the plate is in a mobile liquid condition the globule becomes rapidly flattened by the stronger surface tension about the edges and in a short time hollows out to a new crater. The frequent falling of globules will produce a coarse, bulging ribbed weld. If they fall on a plate whose temperature is too low for the spreading action of the surface tension the result is a poor weld. "The metal didn't bite in."

[5] Professor, University of Vermont, Burlington, Vt.

Mr. Eschholz estimates the importance of vapor action by "guessing at half of the answer and multiplying his guess by two." His result is not without significance, and it is a very important point. If he can prove that the heat required for vaporization is greater than that supplied by the arc in good welding and available for the purpose he will be able to add another contribution to our conceptions of the possible actions of the welding arc.

I wish to thank Mr. Eschholz for his paper, I have found it full of suggestions, and it is a commendable attempt to disentangle very complicated phenomena. In spite of all the work that has been done on the arc, the end is not yet in sight, but such papers as these are helpful and I should be pleased to hear more of them.

A. M. Candy[6] (*Communicated*): Mr. Eschholz only touches very briefly upon arc stability and the exacting requirements of a welding generator which will produce a thoroughly satisfactory characteristic without the necessity of a ballast resistance in the arc circuit. As Mr. Eschholz pointed out, the conventional type of drooping voltage characteristic generators (shunt, compound, differential self-excited, or differential separately excited) is too sluggish to consistently follow the changes of arc resistance which are continuous and instantaneous, and must, therefore, be assisted by a relatively large amount of external inductance. If sufficient inductance is placed in the circuit of the poorest of these generators, the arc can be stabilized to the point that it can be lengthened to an inch or more without rupture, assuming that the surrounding air is reasonably quiet. Under these conditions, however, we find that the fusion of the metal is more or less incomplete, especially at the anode which is the relatively large body of metal to be welded.

In an endeavor to improve generator circuit characteristics to the point requiring no, or at least very little, external inductance, and to minimize the magnetic lag and undesirable transient mutual induction phenomena (unavoidably present in any compound wound—differential or accumulative—direct current generator operated at rapidly and widely varying potentials) the unique scheme of interconnecting the constant potential exciter to the variable voltage generator and providing an inherently automatic

[6] General Engineer, Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

reversing field, was finally evolved as indicated by Fig. 13, in Mr. Eschholz's paper.

This scheme permits the generator to be used either without, or with, a relatively small reactor. The generator is provided with the usual commutating winding, a relatively small series winding, and two field windings, one of which is separately excited, being connected through the variable rheostat (V. R.) directly to the exciter terminals. The other field winding, namely, the reversing field, is connected through the field resistance R 2 to the generator terminals. The negative terminal of the exciter is connected to this field winding, whereas the positive exciter terminal is connected through the interconnecting resistance R 1 to the positive generator terminal. The series winding always opposes the separate winding. When the generator is operating under no load (open circuit) and under normal welding conditions, the current through the reversing field is obtained from the generator terminals in direction indicated by arrows marked O and W. Under these conditions, this field is self-excited and is assisting the separate field to maintain the generator terminal voltage. When the terminals of the generator are short-circuited, however, as in striking the arc, then the current through the reversing field comes from the exciter circuit through the interconnecting resistance, thence through the wire connecting points A and B, as indicated by arrow marked S; thence through the arc circuit and the reversing field in direction of arrow marked S; and thence to exciter. In this case, the reversing field opposes the separate field, thereby assisting the series field in limiting the permanent short-circuit current.

Incidentally, the interconnected scheme prevents reversal of generator polarity even though the exciter circuit becomes accidentally opened. This is due to the fact that not only is the reversing field circuit left intact as a self-excited field, but also the separate field becomes a self-excited field, one end being connected to the reversing field terminal and the other end through the variable rheostat and interconnecting resistance R 1, to the generator terminal at B.

Another advantage of this scheme is the fact that the current delivered to the welding circuit can be varied over the entire range of 50 to 225 amperes by simply turning the contact arm of the

variable field rheostat V R, thereby eliminating the necessity of variable shunts or taps on the series field windings.

Another advantage illustrated by Fig. 15 is that the permanent short-circuit current is very little, if any, greater than normal welding current, especially for values of 150 amperes or less, as a result the tendency for the electrode to freeze to the work when striking are arc is materially decreased. This feature is of particular value to a candidate just learning to weld, and for overhead welding even by an expert operator. If on the other hand, the generator has volt-ampere characteristics as per attached (Fig. 17), we observe that for a normal welding current of 150 amperes at 20 volts, the permanent short-circuit current is about 210 amperes or 40 percent above the normal. This will cause the end of the electrode to reach a temperature above that desired, which makes it fuse to the work more quickly, thereby making it more difficult for the operator to withdraw it just the proper distance (about ⅛ inch) to hold the arc and not withdraw it suddenly such a distance that the arc cannot be held.

Another decided advantage of the characteristic per Fig. 15 over that of Fig. 17 will be found in connection with work requiring the operator to shift from "downward" to "overhead" welding and vice versa. When welding downward, the average operator will not hold his arc shorter than 20 to 22.5 volts. Overhead welding, however, is very exacting in that the operator must continually hold his arc just as short as possible, namely, between 18 to 15 volts. Now in the case of Fig. 15, the arc current is substantially the same at 15 to 20 volts. In case of Fig. 17, however, if the operator requires 125 amperes, he can obtain practically that value at 20 volts per curve A for downward welding. However, if he shifts to overhead work holding a 15-volt arc, he will get approximately 140 amperes, which in most cases will be too much for work requiring 125 amperes. Therefore, he must go to his generator and readjust the control devices (switches or field rheostat or both) until the machine works on the curve B shown in broken lines, whereupon he can get 125 amperes at 15 volts.

To illustrate the beneficial effects of the reversing field, let us consider first the relative ampere turns developed by the different windings under an adjustment for a given welding current, say

100 amperes. When the arc is being operated at 22 volts, we will consider the total accumulative excitation produced by the separate and reversing field as 100 percent, out of which 71.7 percent is supplied by the former and 28.3 percent is supplied by the latter field. Now when the generator is short-circuited, the total accumulative excitation is reduced to 71.7 percent, namely, the separate field, whereas the total differential excitation is 34.5 percent, out of which 17.9 percent is supplied by the bucking series field and 16.6 percent is supplied by the reversing field. In other words, the latter field has changed from 28.3 percent. accumulative to 16.6 percent differential excitation, and is of almost as much assistance as the series field itself. To be exact, it is almost 93 percent of the series excitation.

Furthermore, when the electrodes are touched together and quickly separated (for starting the arc), the current from the constant potential source (exciter) through the welding circuit (and reversing field) is a very decided factor in initiating ionization and electron emission, which is of very material assistance in striking the arc during the short time interval required for the generator to build up its magnetic circuit and establish its terminal voltage, subsequent to removal of the short-circuit condition incident to touching the electrode to the work.

The arc readily obtained from this machine is therefore very tenacious in that it is remarkably stable for all reasonable lengths up to a maximum of 3/8 inch, and also produces deep fusion in the work being welded, which is essential for producing strong welds.

Thos. M. Hunter[7] (*Communicated*): A number of points are brought out in this paper which are a great deal of interest to those who have followed previous investigations of arc welding. Stability of the arc, fusion, and deposition are cited as being three most important factors in making good welds, and it is noted with interest that Mr. Eschholz has found deposition and fusion can be obtained with alternating current as well as with direct current. This fact has been under considerable discussion and many investigators have declared that good welds could not be made with alternating current. Various theories have been advanced to

[7] Transformer Engineer, American Transformer Co., Newark, N. J.

show why better welds are obtained with direct current than with alternating current, and most of them have ended with the apparent conclusions that the direct current arc was better for obtaining the proper fusion and deposition. Evidently Mr. Eschholz has found that practically these factors which enter into the requirement for good welds can be satisfactorily accomplished with either method.

I wish to disagree with Mr. Eschholz's statement that the arc cannot be stabilized with alternating current. My experience has shown that with proper characteristics in the circuit a stabilized arc can be obtained. Of course, the alternating-current arc acts differently than the direct-current arc, and one who sets out to stabilize the arc must become acquainted with alternating current before conditions can be produced which will give the proper characteristics. This, I think, accounts for not only Mr. Eschholz's opinion, but others who have formed similar conclusions. As in a great many other applications of electricity, direct current was found to be easier to adapt and all the early machines were made for this method, and only in recent years have attempts been made on a large scale, to utilize alternating current transformers for supplying power to arc welding systems.

The stability of the arc is also affected to a great extent by the operator. Some operators seem to be able to hold a stable arc under very adverse conditions so far as the characteristics of the circuit are concerned; and others, under the best of conditions, have difficulty. In developing an arc welding transformer some years ago, many experiments were made which continued over a period of several months. While conducting these experiments it was necessary to utilize various operators from the demonstrating department, and I noted that quite a wide variation in results was obtained due to different opinions expressed by the various operators, and it was finally concluded that if consistent results were to be obtained, we must conduct experiments with the same operator. It is, therefore, my belief that the distinction between the methods in so far as the stability of the arc is concerned, is largely psychological and that the operator has as much to do with the stabilizing of the arc as the method employed.

Mr. Eschholz is in error when he states that most of the com-

mercial systems are direct current. This statement would have been true about three years ago, but since that time there has been a very large number of alternating-current transformers sold for arc welding and are being used every day commercially.

On page 267 of the paper is given a very interesting analysis of the division of energy between the anode and the cathode. The anode drop is given to be approximately 9 and the cathode approximately 7, while 2 volts is utilized in the arc. This means that approximately 25 percent greater energy is in the anode than in the cathode. When direct current is used for welding with the positive terminal on work and the negative on electrode, there will be 25 percent more energy in the work than in the electrode, whereas with alternating current the energy in the two are approximately equal, all other things being the same, the work loses 12.5 percent and the electrode gains 12.5 percent of the D. C. energy when alternating current is used.

Based upon these theoretical deductions, the work is usually made positive and the electrode negative, if the direct current system is used, and it has been claimed that due to the 25 percent greater heat in the work, the direct current method is more efficient than alternating current. When we take into account the losses in actual practice which are common to both methods, such as radiation, conduction, and convection losses of heat, the 12.5 percent, which is the real difference in heat at the work, between the D. C. and A. C. methods, is not worth considering. Furthermore, if over-all efficiencies are to be considered, the alternating current method is much superior since an alternating current transformer is more efficient than a motor-generator set. It is, therefore, my opinion that in so far as the difference in efficiency is concerned, it is in favor of the alternating-current method.

A. R. Allard[8] (*Communicated*): The author has undoubtedly contributed a valuable presentation of important observations bearing on the welding arc. Further research should add to the knowledge of the subject without, however, detracting from the value of that already given or without greatly altering the main facts and conclusions.

[8] Welding Dept., Westinghouse Electric & Mfg. Co., Pittsburgh, Pa.

Mechanism of Metal Deposition.

The transport of globules or particles of molten metal from the fusible electrode to the opposite plate terminal, can be clearly recognized if one accustoms himself to the environment of the welding arc and employs a suitable combination of colored lenses—two ruby glasses with an intermediate blue glass gives a satisfactory color and intensity for observational purposes.

Globular formation is very difficult to detect when an extremely short arc is held. However, with a long arc length the size of the globule is sufficient for its ready discernment. Under this condition, continual globular formation is at once evident at the end of the deposition electrode. The formation of the globule does not proceed in a quiet orderly manner over the entire face of the electrode end, but; due perhaps to irregular liquefaction and energy concentration, the globule is in rapid movement, constantly changing its position. When a long arc is held, this agitation is sufficient to throw the metal several inches from the electrode end, frequently, in a radial direction.

At the anode terminal the molten metal appears also to be in a state of violent agitation, akin to boiling, caused perhaps by the constant shifting in position of the arc terminal and therefore in the zone of energy concentration, as well as by the high degree of energy intensity.

Upon holding a short arc length, the observer may note that as a result of the movement of liquified metal at both terminals, contact occurs between the cathode globule, when it is still small, and waves of agitated anode metal. As a result, the surface tension at the anode pulls the globule from the cathode, causing for an instant short-circuiting of the arc, as described by the author and shown graphically in Fig. 6. With electrodes that have the inherent characteristic of forming small globules this transfer occurs at such a rapid rate as to give the impression to an untrained eye of a continuous flow of metal either in vapor or liquid form. However, both careful visual observation and oscillograph records prove this transfer to be an intermittent phenomenon.

Anode Crater.

The molten metal at the anode terminal, as the author correctly states, is the repository for the globule formed at the cathode and

therefore facilitates securing complete fusion. However, it is not apparent to the writer that a true crater or depression exists, while the metal at the anode terminal functions as the arc terminal unless caused by surface tension phenomena upon welding in re-entrant angles. Upon welding a flat surface, the surface of the anode molten metal appears to have a convex rather than a concave contour. This may be ascribed to the agitation of the molten metal as discussed above and is clearly visible if the profile of the anode is observed at a short distance. Upon breaking the arc, the surface of the molten metal becomes concave due chiefly, apparently, to the contraction of the molten metal and partly to its oxidation, forming the well-known crater.

Metal Transport.

Summarizing this mechanism, we find that the metal at both terminals is in a high degree of agitation. As the volume of molten metal at the cathode increases or its distance from the anode decreases, movement of the metal finally results in their contact. The resulting force of molecular attraction, surface tension, adhesion and cohesion at the point of contact, causes metal transfer and movement over the anode surface in the rear of the arc terminal, thus forming the asterial or bead deposit characteristic of metallic electrode-arc welding.

Gas Evolution and Metal Propulsion.

It appears that the evolution of confined gases is too slow to account for any large propulsive force, but such evolution may be an appreciable factor in affecting the degree of agitation of the molten metal.

Apparently, the propulsive forces at the anode terminal are the greater since more material is sprayed from this source over the weld section. This effect can be evaluated by comparing the performance of the carbon arc with that of the metallic-electrode arc, the amount of projected metal being approximately the same in either case. These observations confirm Mr. Eschholz's conclusions that metal transport is not due in any measure to the propulsive forces generated by confined gases, or to the vaporization of the fusible electrode, but is due essentially to the transfer

of liquid metal assisted by molecular forces and agitation of such metal at the terminals.

O. H. ESCHHOLZ: (*Communicated*): Prof. Slocum's extension of the role of surface tension to crater production provides an additional basis for the interpretation of penetration phenomena. With regard to his comments on the amount of energy required for vaporization of electrode material, it will be noted from the approximate estimate given below, that about 3,200,000 watt seconds are required just to vaporize one pound of iron, whereas the data given on page 267 show that but 1,200,000 watt seconds are available at the negative electrode per pound of metal transferred. It must therefore be concluded that but a small amount, at the most, of metal can be vaporized during the process of metal deposition.

Energy Required to Vaporize One Pound of Iron.

	Calories
Heat in Solid Iron at melting point (1600°C)	300
Heat of Change of State	6
Latent Heat of Fusion	70
Boiling Point, assumed 2450°C.	
Heat in Iron from melting to boiling point	187
Latent Heat of Vaporization	1118
Energy required to vaporize one kg. of iron	1681

Or 3,200,000 watt seconds required to vaporize one pound of iron.

With regard to Mr. Hunter's communication, it should be noted that the stabilization of alternating current arc circuits is not discussed in the paper. It is well known, of course, that such stability may be achieved by the use of series resistance or reactance, etc., and the coating or impregnating of electrodes with arc sustaining materials.

Mr. Hunter appears to confuse thermal and electrical efficiencies. Obviously, larger energy input is required for the liquefaction of the larger volume of metal at the base or parent metal arc terminal, owing to its greater thermal capacity and conductivity, than at the wire metal terminal. Practical as well as theoretical consideration dictates that, with few exceptions, the base metal be

made the positive terminal of the direct current welding arc. Where the energy generated at both terminals is approximately equal, as in the case of the alternating current arc, incomplete fusion may occur owing to the fact that with a given energy input, the metal of the wire electrode will melt at a greater rate than that of the opposite terminal. As a result, it is entirely possible for a considerable portion of the deposited metal to rest unfused on the surface of the base or parent metal of the structure to be welded.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 22, 1921, President Landis in the Chair.

ELECTRIC FURNACES FOR NON-FERROUS ALLOYS.[1]

By H. W. Gillett.[2]

Abstract.

Tabulates in great detail all the electric furnaces now in operation in the United States melting non-ferrous metals, giving the kind of furnace, users, capacity per heat. There are 323 in 144 different plants with a capacity of 193 tons per single heat and using 42,350 kw. Also tabulates the composition of the alloys worked in the different furnaces, and the special work for which each type of furnace is best adapted. Discusses briefly the construction, advantages and disadvantages of each type. [J. W. R.]

Five years ago non-ferrous electric furnaces had to be discussed with the emphasis on hopes. Today the recital of actual achievement in this field is no short story, and while the future undoubtedly holds both improvements for the furnaces now in use and the adoption for specific uses of other types than those now common, yet wide use and a fair degree of standardization has already been attained, as is shown in Table I.

Experimental laboratory installations and inactive or discarded furnaces have been excluded from Table I in order to avoid padding the returns.

In selecting a furnace for service in non-ferrous melting three things have to be considered: The characteristics of the alloys to be melted, the characteristics of the furnace, and the nature of the work, *i. e.* the tonnage desired, the number of hours per day the furnace is to work, and whether various alloys are to be melted in the same furnace.

[1] Manuscript received March 15, 1921. Published by permission of the Director of the Bureau of Mines.

[2] U. S. Bureau of Mines, Ithaca, N. Y.

TABLE I.

Electric Furnaces in Active Commercial Use on, or Being Installed for, Non-ferrous Alloys in the United States, January 1, 1921.

Make	No.	User	Alloy	Capacity Tons per Heat per Furnace	Total Capacity Tons	Kw. Rating	Total Kw.
		Direct Arc Furnaces					
Heroult[1]	2	Driver-Harris Co., Harrison, N. J.	nickel alloys	2	4	800	1,600 [2]
Greaves-Etchell	1	Hoskins Mfg. Co., Detroit, Mich.	"	½	½	300	300 [2]
Snyder	1	Monel Metal Products Co., Bayonne, N. J.[3]	monel	½	½	100	100 [4]
"	1	Chrobaltic Tool Co., Chicago, Ill.	cobalt chromium	⅛	⅜	60	60 [4]
"	3	Haynes Stellite Co., Kokomo, Ind.	"	⅛	⅛	60	240 [1]
"	2	Chicago Bearing Metal Co., Chicago, Ill.	leaded bronze	1	2	400	800 [5]
Total	10	Number of users, 6			7½		2,100
		Stationary Indirect Arc Furnaces					
Rennerfelt[6]	1[7]	Chicago Bearing Metal Co., Chicago, Ill.	leaded bronze	1	1	300	300 [8]
"	1	U. S. Mint, Philadelphia	bronze and silver	½	½	150	150 [9]
"	1	" "	"	1	1	300	300 [9]
"	1	U. S. Mint, San Francisco, Calif.	"	½	½	125	125 [9]
"	1	Bausch Machine Tool Co., Springfield, Mass.	hardeners for Al	⅛	⅛	100	100 [9]
"	1	Hardite Metals Co., Long Island City, N. Y.	nickel chromium	½	½	150	150 [9]
Von Schlegell[10]	1	Chicago Bearing Metal Co., Chicago, Ill.	leaded bronze	1	1	450	450 [11]
"	2	Crane Co., Chicago, Ill.	monel and bronze	3/20	3/10	50	100 [11]
"	1	Sandusky Foundry & Machine Co., Sandusky, Ohio.	bronze	3/20	3/20	50	50 [11]
"	1	Manning, Maxwell & Moore, Inc., Bridgeport, Conn.	"	3/20	3/20	50	50 [11]
Total	11	Number of users, 7			6		1775

Moving Indirect Arc Furnaces—Single Phase[12]

Detroit Rocking	2	Aluminum Mfg. Co., Inc., Detroit, Mich.	brass and bronze	1	2	300	600
"	2	American Bushing Corp., Marysville, Mich.	"	1	2	300	600
"	2	American Manganese Bronze Co., Holmesburg, Pa.	"	1	2	300	600
"	1	Bethlehem Shipbuilding Co., Redington, Pa.	"	1	1	300	300
"	5	C. B. Bohn Foundry Co., Detroit, Mich.	brass bronze and aluminum	1	5	300	1,500
"	2	Bound Brook Oilless Bearing Co., Bound Brook, N. J.	bronze	½	1	150	300
"	1	Bridgeport Brass Co., Bridgeport, Conn.	bronze and copper	1	1	300	300
"	4	Chase Metal Works, Waterbury, Conn.	brass	1	4	300	1,200
"	1	Cleveland Brass & Copper Rolling Mills, Cleveland, Ohio.	"	1	1	300	300
"	8[13]	Detroit Copper and Brass Rolling Mills, Detroit, Mich.	"	1	8	300	2,400 [14]
"	1	Ford Motor Co., Detroit, Mich.	brass and bronze	1	1	300	300
"	1	Ford & Son, Dearborn, Mich.	"	1	1	300	300
"	2	Gen'l Aluminum & Brass Mfg. Co., Detroit, Mich.	"	1	2	300	600
"	1	Gen'l American Tank Car Corp., Chicago, Ill.	"	½	1	150	150

[1] Another Heroult furnace melting nickel alloys is installed at Hiram Walker Metal Products Co., Walkerville, Ontario, Canada.
[2] Three-phase automatic control.
[3] According to Diller, H. E., Foundry standardizes nickel alloy, Foundry, Vol. 48, 1920, p. 210, a two-ton electric furnace is later to be installed at this plant.
[4] Single-phase.
[5] Single-phase, automatic control.
[6] A 1/3 ton 100 kw. Rennerfelt for melting monel, bronze and brass up to 22 percent zinc is installed at the Gerline Brass Foundry Company, Kalamazoo, Michigan, but has not been in service for some time on account of power shortage.
[7] A second one-ton Rennerfelt at this plant has been made over into a Von Schlegell furnace.
[8] Two-phase.
[9] Two-phase; nose tilting and automatic control.
[10] Von Schlegell repelling arc furnace may be operated either as direct or indirect arc furnace.
[11] Three-phase.
[12] A three-phase oscillating indirect arc furnace, the Volta, has been tried out in a one-ton 300 kw. size at the Titanium Bronze Co., Niagara Falls, but that firm has ceased operations.
[13] Four installed, four being installed.
[14] Direct pouring furnaces.

TABLE I—*Continued*

Make	No.	User	Alloy	Capacity Tons per Heat per Furnace	Total Capacity Tons	Kw. Rating	Total Kw.
		Moving Indirect Arc Furnaces—Single Phase—Continued					
Detroit Rocking	1	Lumen Bearing Co., Buffalo, N. Y.	brass and bronze	½	½	150	150 (15)
"	1	Hills, McCanna Co., Chicago, Ill.	"	¼	¼	75	75
"	2	Michigan Lubricator Co., Detroit, Mich.	"	1	2	300	600
"	4	Michigan Smelting & Refining Co., Detroit, Mich.	"	1	4	300	1,200
"	2	Mueller Metals Co., Port Huron, Mich.	brass	1	2	300	600
"	1	Oregon Brass Works, Portland, Oregon	brass and bronze	1	1	300	300
"	1	" " " " "	"	½	½	150	150
"	3	Parish Pool Co., Cleveland, Ohio	"	1	3	300	900 (16)
"	1	Rome Wire Co., Rome, N. Y.	copper	1	1	300	300
"	1 (17)	Standard Underground Cable Co., Perth Amboy, N. J.	brass and Cu	1½	1½	300	300 (18)
"	3	Sherwood Brass Works, Detroit, Mich.	brass and bronze	1	3	300	900
"	1 (17)	Sarachan & Rosenthal, Inc., Rochester, N. Y.	brass	1	1	300	300
"	1	M. Smolensky Mfg. Co., Cleveland, O.	"	¼	¼	75	75
"	1	White & Bros., Philadelphia	brass and bronze	1	1	300	300
"	1	Wheeler Condenser & Engineering Co., Carteret, N. J.	"	1	1	300	300
	57	No. of users, 28.				53	15,900
Booth	3	The full list of users of Booth furnaces is not available, as it is not given out by the makers. Among the users are Cleveland Brass Co., Cleveland, O.; Dearborn Brass Co., Cedar Rapids, Iowa; Dallas City Fdry. Co., Dallas City, Ill.; Fulton-Harwood Brass Works, South Bend, Ind.; Nat'l Bronze and Aluminum Foundry, Cleveland, O.; Michigan Smelt-		1	3	300	900
"	4			½	2	180	720
"	25			¼	6¼	125	3,125
"	8			⅛	2	75	600

		ing and Refining Company, Detroit, Mich.; Muskegon Aluminum Foundry Co., Muskegon, Mich,; Yale & Towne, Stamford, Conn.; Hill Pump Valve Co., Chicago, Ill.; Nordyke & Marmon Co., Indianapolis, Ind.; Prime Mfg. Co., Milwaukee, Wis. Some of the Booth furnaces have automatic control.					
	40	No. of users of Booth furnaces, 35-40.			13¼		5,345
American	1	York Hardware & Brass Co., York, Pa.	brass and bronze	½	½	300	300
Grand total for type	98	No. users of type, about 65.			67		21,545
		Reflected Heat Furnaces					
Baily	1	Acheson Mfg. Co., Rankin, Pa.	brass and bronze	¾	¾	105	105
"	1	Akron Bronze & Aluminum Co., Akron, Ohio	"	¾	¾	105	105
"	1	" " " " "	"	¼	¼	50	50
"	1	Allis Mfg. Co., Milwaukee, Wis.	"	¼	¼	50	50
"	1	American Hard. Corp., New Britain, Conn.	"	¾	¾	105	105
"	1	Anaconda Copper Mining Co., Butte, Mont.	"	¾	¾	105	105
"	1	Atlas Brass Works, Columbus, Ohio	"	¾	¾	105	105
"	2	Buick Motor Car Co., Flint, Mich.	"	¾	1½	105	210
"	2	Burlington Brass Works, Burlington, Wis.	"	¾	1½	105	210
"	2	Capitol Brass Co., Detroit, Mich.	"	¾	1½	105	210
"	1	Chapman Valve Co., Springfield, Mass.	"	¾	¾	105	105
"	1	Coppus Eng. & Equip. Co., Worcester, Mass.	"	¾	¾	105	105
"	1	[17] Claus Auto Gas Co., Milwaukee, Wis.	"	½	½	75	75
"	1	Dayton Eng. Labs. Co., Dayton, Ohio	aluminum	⅕	⅕	105	105
"	2	" " " " " "	brass and bronze	¼	½	50	100
"	1	Deming Co., Salem, Ohio	"	¼	¼	50	50
"	3	Detroit Brass Wks., Detroit, Mich.	brass	¾	2¼	105	315

[15] Automatic control.
[16] Two direct pouring.
[17] Being installed.
[18] Direct pouring, standard furnace, lined for larger charge.

TABLE I—*Continued*

Make	No.	User	Alloy	Capacity Tons per Heat per Furnace	Total Capacity Tons	Kw. Rating	Total Kw.
		Reflected Heat Furnaces—Continued					
Baily	1	Drew Electric & Mfg. Co., Cleveland, Ohio	brass and bronze	¾	¾	105	105
"	1[19]	Evinrude Motor Co., Milwaukee, Wis.	"	½	½	75	75
"	1[19]	Flood City Mfg. Co., Johnstown, Pa.	"	½	½	75	75
"	1	Hays Mfg. Co., Erie, Pa.	brass	¾	¾	105	105
"	1	Keyline Co., Cleveland, Ohio	brass and bronze	¼	¼	50	50
"	1	Kennedy Valve Co., Elmira, N. Y.	"	¾	¾	105	105
"	1	Landers, Frary & Clark, New Britain, Conn.	aluminum	1/10	1/10	50	50
"	2	Lumen Bearing Co., Buffalo, N. Y.	brass and bronze	¾	1½	105	210
"	1	" " " " "	Lumen metal	½	½	105	105
"	1	Miller Pasteurizing Machine Co., Canton, O.	brass and bronze	¼	¼	50	50
"	4	Michigan Smelting & Ref. Co., Detroit, Mich.	brass	¾	3	105	420
"	1	A. Y. McDonald, Co., Dubuque, Iowa	brass and bronze	¾	¾	105	105
"	1	McKenna Brass Works, Pittsburgh, Pa.	"	¾	¾	105	105
"	1	" " " " "	"	¼	¼	50	50
"	2	Metric Metals Co., Erie, Pa.	"	½	1	75	150
"	3	McRae-Roberts Co., Detroit, Mich.	"	¾	2¼	105	315
"	1[19]	W. A. Mills. Port Chester, N. Y.	"	½	½	75	75
"	3	Nolte Brass Co., Springfield, Ohio	"	¾	2¼	105	315
"	1	Oro Metals Co., Los Angeles, Cal.	"	¾	¾	105	105
"	1	H. Orne & Sons, St. Paul, Minn.	"	½	½	75	75
"	1	Penberthy Injector Co., Detroit, Mich.	"	¾	¾	105	105
"	1	Pittsburgh Valve & Fixture Co., Barberton, O.	"	¾	¾	105	105
"	1	Regent Brass Works, Marysville, O.	"	¾	¾	105	105
"	1	Rundle Mfg. Co., Milwaukee, Wis.	"	½	½	75	75
"	1	Springfield Brass Works, Springfield, O.	"	¾	¾	105	105
"	5	Standard Sanitary Co., Louisville, Ky.	"	¾	3¾	105	525
"	1	Sperry Gyroscope Co., New York, N. Y.	"	½	½	75	75
"	1	S. H. Thomson Mfg. Co., Dayton, Ohio	"	¼	¼	50	50
"	2	Union Brass & Metals Mfg. Co., St. Paul, Minn.	"	¾	1½	105	210

Baily	1	Union Screen Plate Co., Fitchburg, Mass.	brass and bronze	½	½	75	75	
"	1	U. S. Copper Products Co., Cleveland, Ohio	brass	¾	¾	105	105	[20]
"	1	U. S. Navy Yard, Washington, D. C.	brass and bronze	¾	¾	105	105	[20]
"	1	Utica Valve & Fixture Co., Utica, N. Y.	"	¾	¾	105	105	
"	1	Westinghouse Electric Mfg. Co., East Pittsburgh, Pa.	"	¼	¼	50	50	
"	2	West Virginia Metal Products Co., Fairmont, West Virginia	"	¾	1½	105	210	[20]
"	1	White & Bros., Philadelphia, Pa.	"	¾	¾	105	105	
"	1	J. B. Wise, Inc., Watertown, N. Y.	"	½	½	75	75	
"	1	Wolverine Brass Works, Grand Rapids, Mich.	"	¼	¼	50	50	
	76	No. of users, 51.			48		6,890	
General Electric	1	General Electric Co., Schenectady, N. Y.	aluminum	1/13	1/13	75	75	
"	1	" " " " "	"	¼	¼	150	150	
"	1	" " " " "	brass and bronze	¾	¾	250	250	
"	1	McNab & Harlin Mfg. Co., Paterson, N. J.	"Aterite"	¾	¾	300	300	
"	1	" " " " " "	"	1⅛	1⅛	400	400	
"	1	U. S. Copper Products Co., Cleveland, Ohio	brass and copper	1⅛	1⅛	400	400	
"	1	Ohio Brass Co., Mansfield, Ohio	brass and bronze	1⅛	1⅛	400	400	
"	1[22]	U. S. Navy Yard, Washington, D. C.	"	1⅛	1⅛	400	400	
"	1[22]	Standard White Metals Co., Elyria, Ohio	aluminum	¼	¼	125	125	
	9	No. of users, 6.			6½		2,500	
Rennerfelt Reverberatory	1	Chicago Faucet Co., Chicago, Ill.		3/20	3/20	75	75	
Total for Type	86	Number of users, 58.			55		9,465	

[19] Being installed.
[20] Nose tilting.
[21] Two 105 kw. furnaces are also used by Metal & Thermit Co., Chicago, for tin recovery. Other Baily furnaces are installed in Canada and Mexico as follows: Canada, Empire Brass Works, 1 105 kw.; Monarch Metal Co., 1 50 kw.; Dominion Steel Products Co., 1 50 kw.; Mexico, G. Amsinck Corp., 2 105 kw.
[22] Being installed.

TABLE I—*Continued*

Vertical Ring Induction Furnaces—Single Phase

Make	No.	User	Alloy	Capacity Tons per Heat per Furnace	Total Capacity Tons	Kw. Rating	Total Kw.
Ajax-Wyatt	3	Ajax Metal Co., Philadelphia, Pa.	yellow brass	1/6	½	30	90
" "	16[23]	American Brass Co., Waterbury, Conn.	"	½	8	60	960
" "	24	American Brass Co., Kenosha, Wis.	"	½	12	60	1,440
" "	1	American Hardware Co., New Britain, Conn.	yellow & red brass	1/6	1/6	30	30
" "	6	Baltimore Tube Co., Baltimore, Md.	yellow brass	½	3	60	360
" "	12[24]	Bridgeport Brass Co., Bridgeport, Conn.	"	⅓	4	45	540
" "	2	" " " " "	"	¾	1½	80	160
" "	1	Buick Motor Car Co., Flint, Mich.	"	½	½	60	60
" "	2[25]	Chase Rolling Mill Co., Waterbury, Conn.	"	½	1	60	120
" "	1	Crane Co., Chicago, Ill.	red brass	½	½	60	60
" "	1	Erie-Buffalo Tube Co., Erie, Pa.	yellow brass	½	½	60	60
" "	1	General Electric Co., Schenectady, N. Y.	"	½	½	60	60
" "	1	Haines, Jones & Cadbury, Philadelphia, Pa.	red brass	½	½	60	60
" "	6	Nat'l Conduit & Cable Co., Hastings, N. Y.	yellow brass	½	3	60	360
" "	1	Raritan Copper Works, Raritan, N. J.	"	½	½	60	60
" "	1	Parish Pool Co., Cleveland, O.	"	½	½	60	60
" "	2	Rome Brass & Copper Co., Rome, N. Y.	"	½	1	60	120
" "	2	Scovill Mfg. Co., Waterbury, Conn.	"	½	1	60	120
" "	1	Speakman Co., Wilmington, Del.	"	½	½	60	60
" "	1	Specialty Brass Co., Kenosha, Wis.	"	½	½	60	60
" "	1	Stamford Rolling Mills Co., Stamford, Conn.	"	½	½	60	60
" "	1	Standard Sanitary Mfg. Co., Louisville, Ky.	"	½	½	75	75
" "	2	Standard Underground Cable Co., Perth Amboy, N. J.	"	½	½	60	120
" "	1	W. A. Clark Wire Co., Bayway, N. J.	"	½	½	60	60
" "	6	West Va. Metal Products Co., Fairmont, W. Va.	"	½	3	60	360
" "	1	Western Cartridge Co., W. Alton, Ill.	"	½	½	60	60
" "	1	U. S. Navy Yard, Washington, D. C.	"	⅛	½	60	60
	98	No. of users, 25.			45		4,635
	70	Planned for prompt installation.			35		4,200
Total	168	.....	.....		80		8,835

	Horizontal Ring Induction Furnaces—Single Phase					
General Electric	1 Hoskins Mfg. Co., Detroit, Mich.	nickel chromium	⅛	⅛	100	100
	Contact Resistance Furnaces—Three-Phase					
Bennett	1 Scovill Mfg. Co., Waterbury, Conn.	brass and copper	5	5	500	500
"	6 " " " " "	"	1	6	150	900
				11		1400
	High Frequency Eddy Current Furnaces					
Ajax-Northrup	1 Baker & Co., Newark, N. J.	platinum	..	..	20	20 [26]
"	1 H. A. Wilson Co., Newark, N. J.	"	..	..	20	20 [26]
"	1 D. Belais, New York City	"white gold"			20	20 [26]
"	1 J. R. Wood & Sons, New York City	gold	..	..	20	20 [26]
"	2 U. S. Mint, Philadelphia, Pa.	silver	..	..	8	6 [27]
"	2 " " " "	"	..	..	16	32 [27]
"	1 Handy & Harman, Bridgeport, Conn.	"	¼	¼	60	60 [28]
	9 No. of users, 6.			¼+		188
	Other Crucible Lift-Out Furnaces					
Baily	1 W. A. Rogers, Ltd., Niagara Falls, N. Y.	silver	1/30	1/30	40	40 [29]
Marsh	2[30] Hoskins Mfg. Co., Detroit, Mich.	nickel chromium	1/20	1/10	50	100 [31]
	3 No. of users, 2			2/15		140

[23] This firm plans to double its Waterbury installation and install 24 furnaces, 60 kw. size, at the Torrington, Conn., plant. Installation of some of these furnaces is under way.

[24] This firm originally used mostly the 30 kw. size. but has changed to a smaller number of higher powered furnaces, and contemplates doubling its present installation when business conditions permit.

[25] This firm plans to install about 30 more 60 kw. furnaces, part of this installation being under way at present. Exact information is lacking as to how many of these furnaces planned for future installation are being installed at present.

[26] Single-phase, crucible lift-out.

[27] Two-phase, crucible lift-out.

[28] Three-phase, nose-tilting.

[29] Single-phase, two crucibles.

[30] These furnaces are used less than formerly on account of the installation of larger furnaces of other types.

[31] Single-phase, one or two crucibles per furnace.

TABLE I—*Summary.*

Make	Total Capacity per Heat Tons	Total Kw.	Number Furnaces	Number Users
Ajax-Wyatt	45	4,635	93	25
Detroit Rocking	53	15,900	57	28
Baily	48	6,890	76	51
Booth	13	5,345	40	35
Other furnaces	34	9,580	52	30
Total in use	193	42,350	318	169
Ajax-Wyatt, planned for prompt installation	(35)	(4,200)	(70)	25 duplicates
Total including Ajax-Wyatts planned ...	228	46,550	388	144 separate users

Table II gives data on the applicability of various furnace types to various alloys. An O. K. in this table does not necessarily mean that it is economically desirable to melt a given alloy in a given furnace—merely that it is metallurgically feasible.

The main important characteristics of brass from the point of view of electric melting are the volatility of the zinc contained in it and the rate of heat conduction through the molten brass. If heat is supplied from above at a more rapid rate than it can be conducted through the melt, overheating of the surface layer ensues and the loss of zinc becomes prohibitive. Hence electric furnaces of the direct or indirect arc types used for steel are not applicable to a brass high in zinc. The ordinary horizontal-ring induction furnace is not applicable because of "pinch" troubles due to the high electrical conductivity of the alloy. Alloys that approach steel in their nature rather than brass, for example the non-volatile nickel alloys, such as nichrome and monel metal, can be and are successfully melted in ordinary direct arc furnaces used for steel, like the Heroult, Greaves-Etchell and Snyder. Nicrome can be handled in the ordinary induction furnace. True bronzes can be melted by a direct arc. Direct arc furnaces of the roof-opening type allow rapid charging and are well-liked in one installation on bronze where rapid production is the chief aim.

Alloys									Types of Furnaces						
Fe	Cr	Ni	Cu	Sn	Pb	Zn	Ag	Al	Direct Arc	Stationary Indirect Arc	Moving Indirect Arc	Reflected Heat	Contact Resistance (Bennett)	Vertical Ring Induction	High Frequency
	15	85	..	..	..	..	..	..	O. K.	O. K.	O. K. ?	? 1	?	?	O. K. ?
5	..	67	28	..	..	..	..	..	O. K.	O. K.	O. K.	? 1	?	?	O. K. ?
		25 5	75 95	.. ..	.. ..	.. ..	.. ..	.. ..	? 2	O. K.	O. K.	O. K.	O. K. ?	?	O. K. ?
			100	..	..	..	..	..	? 2	O. K.	O. K.	O. K.	O. K.	No–3	O. K.
			90 88	10 10	.. 2	.. ..	.. ..	.. ..	O. K.	O. K.	O. K.	O. K.	O. K. ?	? 3	O. K.
			80 76 68	10 3 4	10 18 26	.. 3 2	.. .. ..	.. .. ..	O. K. 5	O. K.	O. K.	O. K.	O. K. ?	No–4	O. K.
			85	5	5	5	..	..	No–5	O. K.	O. K.	O. K.	O. K.	O. K.	O. K.
			74 80 70 67 61 65 60	4 .. .. .. 1	5 .. .. 3 .. 1 ..	17 20 30 30 38 34 40	.. ..	.. ..	No–5	No–5	O. K.	O. K.	O. K.	O. K.	O. K.
		18	58	..	..	24	..	..	No–5	No–5	O. K.	O. K.	?	O. K.	O. K.
			3 2 8 10 10	.. ..	.. ..	15 30 85	.. .. .. 90 ..	82 68 92 .. 5	No–5 ? ? No	? 5 O. K. ? O. K. O. K.	O. K. O. K. O. K. ? No–5	O. K. O. K. O. K. ? O. K. ?	? ? ? ?	? 3 ? 3 ? 3 ?	O. K. O. K. O. K. O. K. ?

O.K. = Furnace metallurgically satisfactory for this alloy.
? = No data on hand.
O.K.? = Probably satisfactory, but no record of trial.
No = Furnace not satisfactory for this alloy.
1 = Temperatures probably rather high for good refractory life.
2 = Question of copper poisoning by fume from direct arc not yet settled.
3 = Induction furnace on this alloy would require resistor tube of special design.
4 = Lead too high for good life of usual lining of induction furnace.
5 = Furnace causes loss of volatile metal from this alloy.

Pure copper ought to be capable of being melted with a direct arc, but according to Hansen's experience doing so caused volatilization of copper and copper poisoning of the workmen. It is probable that this trouble, or the lack of it, depends again on the relative rate at which heat is supplied and that at which it is conducted through the melt. A high-powered arc in contact with the charge evidently causes some volatilization of copper. Less severe and less local heating is obtained in indirect arc furnaces. The U. S. Mint has had fine success on coinage nickel, bronze, and silver, with Rennerfelt indirect arc furnaces.

Silver is slightly volatile, and a direct arc type would hardly be applicable. The indirect arc type is, the U. S. Mint having melted 3,000,000 lb. (1,363,000 kg.) of silver dollars with a metal loss of 0.01 percent.

The new von Schlegell "repelling arc" furnace, which may be operated either as a direct or an indirect furnace, is being applied to non-ferrous melting. If the self-starting and automatic regulating scheme proves mechanically and electrically feasible, this furnace may be of value on those alloys that can be melted in direct or stationary indirect arc furnaces.

When we come to the common red brasses, which contain say five percent Zn the direct arc is not suitable, and at about 20 percent Zn the stationary indirect arc also proves unsatisfactory. When we get to the very important yellow brasses of 30 to 40 percent Zn or to nickel brasses (German silver) we are forced to abandon the standard steel furnace types and strike out on new paths. This necessity has been the mother of a number of interesting and ingenious methods of avoiding the difficulty.

Three general methods have been followed:

(*a*) Using a low rate of power input.

(*b*) Using a high rate of power input, and stirring by moving the furnace.

(*c*) Heating from within the metal itself, with inherent stirring.

A low rate of power input means low efficiency and low production. When the heat is mainly indirectly transmitted from the source to the charge by reflection from the roof in order to distribute it more evenly, refractory problems are made rather

difficult. Various furnace builders attack the problem with furnaces of this general type in different ways.

Bennett builds his furnace like a regular three-phase direct arc furnace, but holds the voltage away down so that he gets contact resistance rather than true arcs, and by holding down the rate of power input, allows time for equalization of temperature and avoidance of local superheating. By generating the heat close to the charge he avoids much of the thermal loss found with other low-powered types.

The largest electric brass furnace in use is of this type, though it has not been introduced into the industry outside the plant of the inventor.

Baily uses a large, relatively low temperature source of heat, a single-phase granular resistor, and still further distributes the heat by reflecting the bulk of it from the roof. A very low rate of power input is used, partly on account of the limitations due to the resistor troughs, and a furnace results which is slow, giving low production, sluggish, with a high heat storage, and of low thermal efficiency, especially when not run continuously. However, the furnace is simple, and easy to operate and has for this reason had a large measure of success.

The General Electric Company's furnace applies heat in much the same manner as the Baily, but by using the smothered-arc or contact resistance principle; it can use a higher rate of power input, gaining somewhat in thermal efficiency, but increasing the difficulties with the refractories due to the higher temperature of the heat source. Three-phase power can be used instead of single-phase. Considering the time it has been on the market, it has found relatively little use.

The Rennerfelt "electric reverberatory" is just like the General Electric furnace in its source of heat, but locates this in the middle of the furnace instead of around the sides, and consequently wastes less energy in heating the furnace walls instead of the charge. One small furnace of this type has shown promising results. If structural difficulties do not become too great in man-size furnaces, it should find considerable use.

The next method of avoiding the specific difficulties found with alloys high in zinc is to use an indirect arc furnace, with a high rate of power input to get thermal efficiency, and to move the

furnace so as to stir the metal and avoid superheating the surface. This was done long ago by Stassano in the early days of electric steel, but such furnaces were not then applied to brass. The principal users of this method are the Detroit rocking furnace (operating under license from the Bureau of Mines) and the Booth rotating furnace, the former being installed almost wholly in the one-ton size, and the latter almost wholly in 500 lb. (225 kg.) or even smaller sizes. These furnaces give good efficiency, even on an eight-hour day, and have been adopted by the industry with remarkable rapidity. They are capable (especially the Detroit, which can be mechanically charged from overhead) of rapid operation and high production.

A similar furnace, the American, has been introduced by Ryan, but only one installation has yet been made. All these furnaces are single phase.

A polyphase furnace, The Moore "Rapid 'Lectromelt" has been advertised for sale and is stated to fall into the moving indirect arc class, but nothing more than experimental operation has yet been credited to this furnace and its details are still shrouded in mystery.

The old gyrating Stassano has very recently been resurrected at the hands of the Volta Mfg. Co., provided with a simpler gyratory mechanism, renamed the "Volta", and applied to brass. One of these furnaces has had a short experimental foundry tryout, but little data are yet available, so the adequacy of the stirring is not yet known. It has the advantages of three-phase operation, but lacks the ability of the rocking type to take up heat from the roof into the melt.

One other possibility deserves mention, though it is not yet in use. The rocking, rotating, or gyrating Thomson-Fitzgerald design has a solid slotted resistor as the source of heat, and the furnace is moved to stir the charge. Though the furnace was once advertised for sale, data on its performance are lacking, and further discussion is not called for here.

We now come to the third method of meeting the idiosyncrasies of brass. Hering's work on the pinch effect was the starting point for those furnaces which use the metal itself as resistor and by virtue of various electromagnetic effects, such as the pinch

effect and the motor effect, cause circulation of the metal. The Hering furnace was tried out on brass on a considerable scale but is no longer in use. Hering has a plan for overcoming the difficulties with the metallic electrodes of the old form of the furnace, and it would be interesting and desirable to have his new scheme tried out, but until it is so tried, comment must be reserved.

Foley has made large-scale experiments on a vertical-ring induction furnace in which the hydrostatic head of the molten metal opposes the pinch force, but at last reports his furnace was not yet in the commercial stage.

The Ajax-Wyatt vertical-ring induction furnace, with its internal heating in the metal itself, its automatic circulation, and its compact form, has shown astonishing thermal efficiency and has been adopted very widely by those brass rolling-mill industries which can readily melt 24 hours a day and need not often change a furnace from one alloy to another—conditions vital to the successful operation of this furnace. As these conditions are seldom found in the foundry, as differentiated from the rolling mill, it has had little foundry use. It is in general not applicable to alloys of high electrical conductivity, *i. e.* those high in copper.

It is rumored that the General Electric Company may soon complete the development of a horizontal-ring induction furnace for both steel and non-ferrous alloys, but data on the progress of the work are not available.

The last type that deserves mention is the Ajax-Northrup, the ingenious high-frequency eddy-current furnace which Dr. E. F. Northrup has already described to this Society. This is in commercial use on silver, platinum, etc., and besides the commercial installations some 25 furnaces are being used in laboratories on account of their extreme flexibility.

The furnace itself is highly successful for its special applications, and may be expected to find large commercial use if and when the generation of the necessary high-frequency current is so developed and cheapened that man-sized Ajax-Northrup furnaces are practical.

It appears that with this array of furnaces any brass melter can find an electric furnace of at least fairly well-proven ability, to handle his work, as there are many types and many sizes of

most types. If he cannot use a single-phase furnace owing to limitations of his power supply, he can probably find a three-phase type that will serve. As a matter of fact, the furnaces in widest use, the Ajax-Wyatt, Baily, Booth, and Detroit, are all single-phase.

If the furnace is chosen so as to be metallurgically fit for its work, for example, if a direct arc or a stationary indirect arc furnace on yellow brass is avoided, and if they are run closed when melting yellow brass so that zinc vapor does not escape, all the furnaces show marked savings in metal losses. Labor costs are low, as the furnaces either require little attendance or can be supplied with automatic control and the writer believes they will be increasingly so supplied.

Power costs are a function of the price of power, the continuity of use of the furnace, and of the thermal efficiency of the furnace. At war-time prices for fuel, electric melting was cheaper on nearly all non-ferrous alloys in nearly all locations, with almost any electric furnace. With fuel prices nearer normal the innate thermal efficiency of the furnace and the operation of a given furnace as nearly continuously and with as few delays as possible, so as to develop the highest possible thermal efficiency, will become increasingly important.

When the electric furnace replaces crucible furnaces it effects a large saving in that item. In calculating the savings possible by electric melting, one should not forget, as some electric furnace salesmen are prone to do, that the electric is high in first cost and that interest, depreciation and obsolescence charges cannot be disregarded. These charges, per ton, are minimized by operation that gives maximum production, *i. e.* steady operation on 24 or 16 hour schedules instead of 8 or 10, cutting down delays in time of pouring and charging, and keeping up to the maximum allowable rate of power input.

The most important of all points about any furnace, its ability to produce metal of the desired quality, has not been mentioned, because without it, no furnace can be used.

It is doubtful if the electric has produced any better brass than the best from the old crucible in a pit-fire, but due to the larger melts and the stirring produced by some furnace types,

electric brass is probably more uniform and more uniformly good than that from fuel-fired furnaces.

The list of users in Table I is sufficient proof that the electric brass furnace gives a good quality of product. This same list, better than any other evidence, proves too that electric melting of non-ferrous alloys is commercially economical.

The electric brass furnace today occupies a position of greater relative importance in the brass industry than the electric steel furnace does in the steel industry, and has reached this position in a much shorter time.

Of commercially important non-ferrous metals and alloys other than brass and bronze there have already been mentioned the nickel alloys, silver and platinum. Aluminum remains to be considered. The electric melting of aluminum has not progressed as far as that of brass and bronze. The large latent heat of fusion of aluminum makes it require a good deal of energy for melting, theory calling for twice as much energy to melt aluminum and heat it to pouring temperature as to melt and heat yellow brass to its much higher pouring temperature. Hence production is slower on aluminum than on brass. Moreover, at these low temperatures fuel-fired furnaces are relatively more efficient than they are at higher temperatures, so that the electric furnace has stronger competition. A large Baily furnace has been tried out on the preparation of aluminum alloy ingots and worked well on aluminum zinc alloys, as it reduced zinc loss. But there is not a sufficient tonnage of Al-Zn alloys used in the country to keep this furnace busy, and as it did not show any advantage on other aluminum alloys it was discarded. A smaller Baily was tried by another ingot producer and also discarded.

Several aluminum foundries use Baily furnaces on aluminum, however, and the General Electric Co. uses its furnace for that purpose. The Detroit has also given good results on aluminum. The General Electric Co. is developing an aluminum furnace with a Ni-Cr resistor which ought to be feasible at the temperature involved and its use should throw light on the interesting question of whether a more or less reducing atmosphere, as in a carbon resistor or arc furnace, or an oxidizing one, as in the Ni-Cr furnace, is the better for aluminum.

On the usual aluminum alloys the electric furnace does not show any particular saving in metal. Its economical use in comparison with fuel-fired furnaces will depend on prices of fuel and of power. It is of service where close temperature control is essential.

Cathode zinc has been melted in a 1,000 kw. Baily furnace, but the furnace was not found satisfactory and was discarded.[3]

Baily furnaces of 100 kw. are, however, successfully used in the production of "Lumen" metal, an alloy of 85 percent Zn, 10 Cu, 5 Al.

For alloys of still lower melting points, Babbitt, solder, type metal, etc., there are metallic resistor furnaces, but they have found little use.

Electric melting, then, is thoroughly established on brass, well established on bronze, common on nickel-chromium, and similar alloys, growing on silver and other precious metals, has a foothold only in aluminum, and is unusual on lower melting alloys.

There are possibilities for greater use of the electric furnace on some of these alloys, and perhaps, though this seems doubtful, in the large scale melting of cathode copper. Instead of any further spectacular extension of electric melting to other non-ferrous alloys, the immediate future seems to promise merely a gradual growth, electric furnaces finding new applications in specific cases from time to time rather than all at once and in an industry as a whole, as was the case with brass.

Discussion of "best practice" in non-ferrous electric melting in general is impossible, because best practice depends on what alloys are to be melted, in what furnaces they are to be melted, and on many varying plant conditions. A special technique, though one readily acquired, is needed for each furnace under each set of conditions, so no attempt will be made here to state whether the night watchman should turn the current onto a Baily furnace at midnight or at 4 A. M., in order to get it properly preheated for the day's run, or whether a one-ton Detroit should start rocking after 75 or 100 kwh. has been used on a given heat. There are interesting possibilities in preheating the charge by fuel before putting it into the electric furnace, and in the use of two furnaces with one

[3] Causes for failure of this furnace are given by F., Laist, Mining and Metallurgy, Bulletin No. 1028, 1920, p. 34.

set of electrical equipment, so that one furnace is melting while the other is pouring and charging, and the electrical equipment is kept busy all the time, the load factor kept up and the maximum demand cut down. These ideas will undoubtedly work out in specific instances, but not in all.

Such points have to be solved by the past general experience of the maker of the furnace selected plus the user's specific knowledge of his own conditions and his own problems.

The fundamental requirement for good performance of an electric furnace on non-ferrous alloys is that the furnace be fitted for its job. Under some plant conditions half-a-dozen different furnaces might give equally good results, more commonly only a couple ought to be considered, often one is pre-eminently suitable, and sometimes (but in the case of brass and bronze very rarely) no electric furnace can properly compete with the most suitable fuel-fired furnace. Nevertheless, experience has shown that an electric furnace, metallurgically suited to its job, once installed generally stays in service, even though the melting cost sheets may show no saving. That is, the advantages of ease of control, cleanliness, and less trying working conditions for the furnace tender, which can hardly be expressed in terms of dollars and cents, are as real reasons for the adoption and use of electric furnaces as the more obvious reason that it generally costs less per unit to melt in the electric furnace.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 22, 1921, President Landis in the Chair.

ELECTRODYNAMIC FORCES IN ELECTRIC FURNACES.[1]

By Carl Hering.[2]

Abstract

A number of recently discovered mechanical forces are described which are of electric origin and which may be made use of, or may be detrimental, in some types of electric furnaces, chiefly those in which the heat-developing resistor is a liquid, which responds to these forces more readily than a solid. Such forces may be usefully applied to cause the liquid metal to flow very rapidly through the heat-developing resistor, thereby enabling the furnace to be forced, and to cause a strong upward circulation in an adjoining bath, by which the metal is refined of suspended impurities and made homogeneous. After referring briefly to the formerly-described "pinch effect," a description is given of the "stretch effect" and of the "corner effect," known also as the "motor effect."

In electric furnaces in which the materials to be treated are in liquid form, like molten metals, it is being recognized that a circulation which is far more rapid than the slow one due to gravity is often desirable since it makes the mass more homogeneous, which is generally very important in the case of alloys, and modern steels are very sensitive alloys. If directed upwards the circulation refines the metal of suspended impurities; it sometimes enables the furnace to be forced, which means a smaller furnace for the same output, and it enables the heat to be distributed more rapidly and more evenly throughout the hearth.

If the forces which produce such circulation can be generated

[1] Manuscript received March 3, 1921.

[2] Consulting Elec. Eng., Philadelphia, Pa.

simply, cheaply and more effectively by the furnace current itself, that is, electrodynamically, instead of by some mechanical stirring paddles, rocking devices, etc., it is an evident advantage. It is the purpose of the present paper to describe briefly some of these newer electrodynamic forces.

In a paper read before this Society in 1907[3] the writer described a peculiar electrodynamic force which sharply limited the current which it is possible to send through a liquid conductor, like molten metal in an open channel in an electric furnace. On increasing the current in such a conductor a limit was reached at which the metal conductor at some one point (always where the cross section is smallest) became depressed, forming a sort of valley, which when it extended to the bottom broke the circuit; in appearance it acts as though it were being pinched off by a powerful invisible pinchcock, and for this reason the writer colloquially called it the "pinch effect," a name which has adhered to it and by which it is now generally known in this country and abroad.

This name has been termed a misnomer by the author of a recent article, and, as the present writer gave it this name, he wishes to say in defense, that though unscientific, it describes, in one word, better than any other one word, the way the phenomenon manifests itself in practice in rupturing a liquid circuit, which it always does only in one point, like in tearing a rope, and almost precisely as a column of liquid in a rubber tube is broken by the usual pinchcock. The term was at first used only colloquially, but it came into use so rapidly that it would have given rise to confusion to have changed it; no better term has been suggested during the fourteen years that it has been used.

The phenomenon may be explained popularly as being due to the magnetic flux which encircles any current-carrying conductor, and which when sufficiently intense tends to crush the conductor with a radial force acting from the periphery towards the center, like a strongly stretched rubber ring around a yielding rod; liquid conductors easily yield to this force and are thereby put into motion. It is now well known that it is this force which makes it impracticable, if not even impossible, to use the ordinary

[3] Trans. American Electrochem. Soc. (1907), **11**, 329.

open-channel induction furnace for good conductors like copper, aluminum, brass, etc., in which the heating currents must be very large because the resistivities are small.

The law stated in all books on electricity that "like currents attract," has been offered to explain this crushing force, but this phenomenon proves this law to be wrongly stated, as it is not the currents but the material of the conductor which is acted upon by this force. Were this law correct, the pinch effect would not exist, and the current density in a conductor would be greater at the center than near the circumference, which we know is not the case. Moreover "like" currents having no conductors, as in the case of the cathode rays, in fact repel each other, as they theoretically should, if they are constituted by the motion of like charges.

The pinch effect has a stable and an unstable region, as has been described by the writer.[4] As the current in an open channel is increased a depression or valley is first formed at the point of smallest cross-section; this action will go no farther if the current then remains constant. With greater, though constant, currents this depression deepens until a depth is reached (roughly at half that of the trough) at which the unstable state is reached, and it then automatically gets deeper until the circuit is broken. With a slowly increasing current, therefore, a warning is given before the break occurs.

There are numerous other phenomena allied with this pinch effect, among which may be briefly mentioned the following: external magnetic fields, such as those produced by magnets or neighboring currents, sometimes have very marked effects on it; a permanent magnet increases the effect enormously, when direct currents are used. A bar of iron held above an open channel causes the liquid conductor to rise up under it, forming a little hill instead of a valley; when held below it very greatly increases the force of the pinch effect. In a liquid conductor consisting of different materials the pinch effect forces the best conducting material to the central axis of the conductor. Thus a copper wire, which ordinarily floats on mercury, will submerge instantly when a strong current flows through the mercury. This action tends to

[4] Trans. American Electrochem. Soc. (1909), **15**, 255.

separate metals from their suspended impurities like slags, oxides, etc., in the furnaces based on this phenomenon, and undoubtedly is one of the explanations of the refining action which is known to take place, as it is found that these impurities are squeezed out, as it were, and gather on the linings of the resistor holes. The shape of conducting particles suspended in a liquid conductor may cause the pinch effect to move them in the direction of the axis of the main conductor when, due to the shape, the pressure produced by the pinch effect is greater on one side than on the other. Thus Northrup has shown that a piece of copper pointed at one end and rounded at the other, when floated on mercury, will move toward the rounded end. Conical resistors may cause the flow to be greater in one direction than in the other. Any mechanical motions produced by the pinch effect must of course appear in the electric circuit as a counter e. m. f. representing the amount of mechanical energy; in one furnace the writer found that as much as about half the total energy was thus converted into the motion of the liquid, which, by friction, is then converted into heat. This is not surprising, as it ought to take considerable energy to start large masses of heavy metals into rapid motion.

The application of this pinch effect to a type of electric furnace, to cause rapid circulation through the resistors, thereby enabling the furnace to be forced, has been described by the writer in several papers.[5] In these the rupturing of the circuit is prevented by the hydraulic pressure produced by the overlying metal, and the force produced by the pinch effect is utilized to produce a rapid flow of the metal through the resistor, thereby rapidly carrying the heat into the main bath. Many of these pinch effect furnaces are now in daily use.

To the user of this type of furnace it is of no interest whether this motion in the direction of the axis (hence perpendicular to the radial pinch-effect pressure) is a true primary electrodynamic force or a secondary effect due to hydrostatic forces, which can turn corners; just as in electrolytic operations, it is of no special interest to the user whether a desired result is a primary or a secondary reaction. The user is interested only in the fact that this flow of liquids exists and is available in furnaces.

[5] Trans. American Electrochem. Soc. (1911), **19**, 255.

Some physicists believe that the only possible electromagnetic force which can act in or on any current-carrying conductor is always exactly perpendicular to the axis of the conductor and can therefore never act to move the conductor in the direction of its axis. But the fact that such a movement does exist in these furnaces requires an explanation, and they explain it by the fact that it is hydraulic in nature and therefore can exist only in liquid conductors and not in solid ones; the radial force of the pinch effect forces the material to the central axis of the conductor, causing a higher pressure there, and by hydraulic action this pressure causes the liquids to flow lengthwise through the conductor. As one or both ends of this resistor, in these furnaces, opens out into the hearth or hearths, the material of the conductor is forced out of these ends, other material entering around the circumference to take its place.

To avoid this bi-directional flow of the metal through the resistor, which may sometimes have some disadvantages, the writer showed that a double hearth[6] may be used as shown diagrammatically in Fig. 1, connected by the resistor, and by rocking the whole furnace slowly, making each hearth alternately the higher one, the flow can be made undirectional, as the pinch effect will act to expel the metal in that direction which offers the least mechanical resistance.

In the C. G. S. system of units used by the physicist, the writer has shown[7] that quantitatively the formula for the pressure produced by the pinch effect is a simple and easily remembered unit relation, namely $P = I^2/S$, in which the pressure P at the center section is in dynes per square centimeter, the current I is in C. G. S. units (ampere $\times$ 10), and the cross section S is in square centimeters.

The writer has shown[8] that there are good reasons to believe that there exists also a true electrodynamic force which he has colloquially called the "stretch effect," which tends to stretch a conductor when the current flows through it. A current-carrying conductor would thereby tend to lengthen itself, and therefore tend to move in the direction of its axis. This would explain the

[6] U. S. Patent No. 1,162,773, filed May 1, 1913, Figs. 1 and 3.
[7] Metallurgical and Chem. Eng., Feb., 1911, 9, 86.
[8] The Stretching of a Conductor by Its Current. Journal of the Franklin Institute, Jan., 1911, p. 73.

well-known rising of the metal on the outer side of the ring of an ordinary induction furnace, and would explain the flow in a pinch effect furnace as being the result of a direct electromagnetic force and not indirectly as the result of hydraulic forces. The pinching and the stretching forces are complementary in nature

Fig. 1

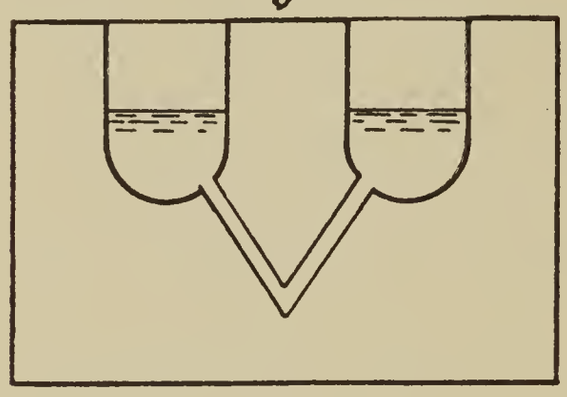


Fig. 2

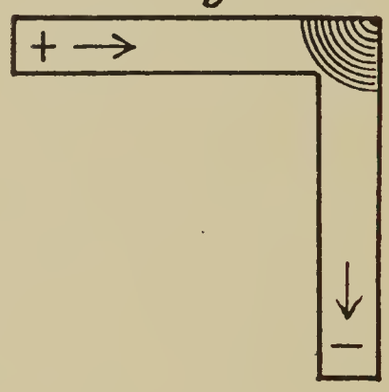


Fig. 3

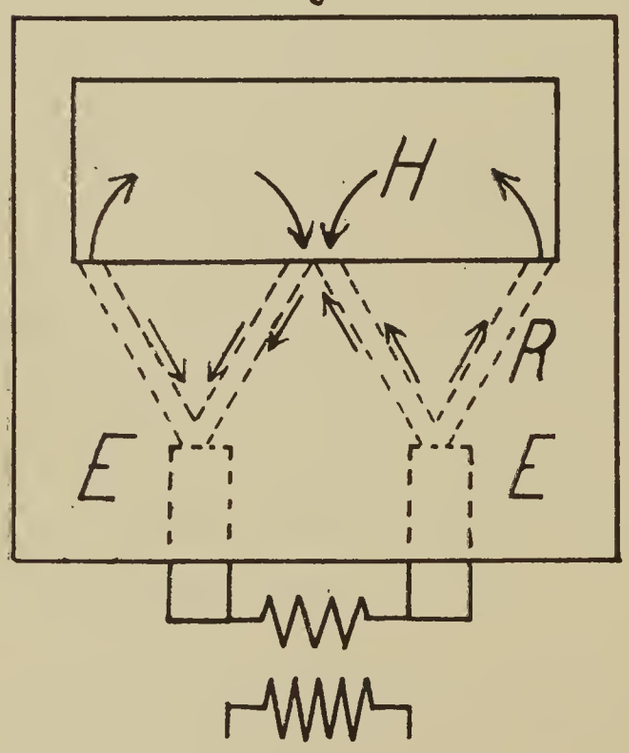
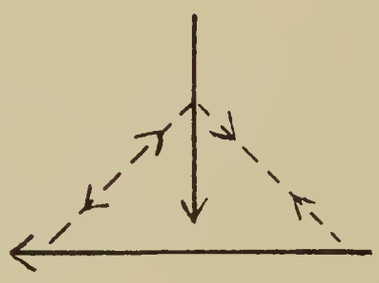


Fig. 4



and go together; the observed results may be explained by either. They may both act together, or one or the other may be made the more effective one.

Owing to the fact that no electromagnetic forces were generally known in the past other than those which act perpendicularly, the views of the writer concerning this stretching force have

apparently not been generally accepted by physicists, though on the other hand, during the ten years since that article was published, no one has shown conclusively that such an axial force cannot possibly exist, except on the ground that it was not known in the older art, which reason the writer does not consider sufficient.

Whether or not these axial forces, which do exist and are available in furnaces are really electrodynamic or only hydraulic, is merely of interest in explaining the theory of the phenomena, and of no consequence to the user of such forces.

More than a dozen years ago, while the writer was conducting researches with these odd high-current-density phenomena, he noticed that when a strong current was passed through an open channel of mercury which turned a right-angled corner, as shown in Fig. 2, the mercury was strongly agitated at the corner by currents that were too small to produce a rupture by the pinch effect in the rest of the open channels. Evidently some strong forces existed in the corner, or at least manifested their existence there. The writer colloquially termed it the "corner effect," and concluded that the forces causing it were due to the electromagnetic effects of the current in each side of the angle on that in the other side; the single current may for this purpose be considered as two currents, one flowing toward the angle and the other from it therefore called "unlike currents."

A number of years later this corner force was re-baptized by others[9] who gave it the name of "motor effect," which if carefully considered is a misnomer as a distinguishing name, because all these several forces which cause a movement of the conductor are equally entitled to be called motor effects.

This curious effect of two currents making an angle with each other was described by the writer to his young assistant, James Wyatt, a short time later, also to Dr. E. F. Northrup, and to Mr. G. H. Clamer, of the Ajax Metal Co., and a furnace was at that time designed by the writer and constructed at the works of the Ajax Metal Co., in which this corner effect should, according to the writer's tentative theory, give the much desired unidirectional flow through the resistors of a pinch-effect furnace. The

[9] Clamer, Journal Franklin Inst., Oct., 1920, p. 491.

subsequent operation of this furnace tended to prove the correctness of the theory; it operated as prophesied.

This furnace is shown diagrammatically as a view from the top in Fig. 3. *H* is the open bath of metal, *E E* are the electrodes and *R* the four resistors making angles with each other as shown, and consisting of the metal in holes through the lining reaching to the electrodes and submerged below the level of the bath *H*. The directions of the currents are shown by arrows next to the resistors and the directions of the flow of metal by arrows in the hearth *H*. The latter forces were very marked and were evidently quite strong; they were always in the directions shown and were not merely a matter of accident as to how the metal happened to start to flow. The force of this unidirectional flow is so great that when the level of the liquid in the bath was only about half an inch above the lateral openings of the holes, in a lead furnace, the suction at the middle holes was so great as to draw in some air, causing a snorting sound. This furnace was exhibited in operation, before this Society at its Niagara Falls meeting in 1914.

The writer's tentative theory was that since "like currents attract and unlike repel," according to the laws as stated in books, there should be a component of this force acting on the conductor in the axial direction when two currents are inclined to each other. The algebraic sum of these axial components in the so-called "W" furnace, in Fig. 3, ought then to give this unidirectional flow. A trial showed that the predicted flow existed in fact.

The chief feature of interest to furnace engineers is that these currents inclined to each other also give rise to some strong forces which have a definite longitudinal direction, independent of whether the current is direct or alternating. Different opinions exist as to a theory to explain this force. But the furnace engineer is more interested in the fact that this peculiar force exists, and less in the theory of it, which belongs more properly to physics, and will therefore be discussed in another paper intended for physicists.

Briefly, however, it may be said that in this case again some physicists insist that such electromagnetic forces can act only perpendicularly to the conductor, and can therefore never have a com-

ponent force in the longitudinal direction; they base this on the fact that no axial force has ever before been shown to exist. The writer's experiments, which show the existence of such forces, they explain by saying again it must be a hydraulic action,[10] therefore secondary in nature and not electrodynamic; in hydraulics such forces can turn corners.

The writer has found, however, and will show elsewhere, that solid conductors are also moved in these axial directions when two currents make an angle with each other, hence the conclusion that the action m u s t be hydraulic and cannot possibly be electromagnetic, is in error, as there cannot, of course, be any hydraulic action in solids.

Moreover, the explanation of this corner effect, now known as the "motor effect," as originally given by the writer in the first published description,[11] is based on the same theory as that given for such angular currents in that well-known and much-used text-book, Ganot's Physics, 8th Ed., p. 740, hence cannot be calmly dismissed as wrong by lesser lights, without more proof than a mere opinion. The fact that such axial forces have not been known before to physicists, is in the writer's opinion not a proof that they cannot possibly exist.

Based on this Ganot diagram, the forces between two currents at right angles is approximately along the d i a g o n a l dotted lines in Fig. 4, repelling on the left and attracting on the right. Being along a diagonal, they must necessarily have components along the axes of the conductors. These longitudinal forces are t o w a r d the intersection when the currents are "alike" (both flowing toward or away from the corner), and a w a y from the intersection when the currents are "unlike" (one flowing toward and the other away from the corner). This is what is found to take place in Fig. 3, in which the two halves of Fig. 4 have been practically separated, the currents turning the corner or meeting at the corner.

An experimental apparatus (believed to be attributed to Faraday) existing in many physical lecture laboratories, and of which this diagram in Ganot is the explanation, shows that the

[10] Nature and Explanation of the "Motor Effect" in the Ajax-Wyatt Furnace. By E. F. Northrup. Jour. Franklin Inst., Dec., 1920, p. 817.

[11] U. S. Patent 1,105,656, filed July 15, 1911, Figs. 1 and 2.

two forces when combined will move the vertical conductor parallel to itself, when it is mounted so that this is the only direction in which it can move. As this force is exerted between the two conductors, it seems very evident that if the vertical wire in Fig. 4 is made the stationary one and the horizontal one is mounted so that it can move only in the direction of its axis, it will do so, thereby showing the existence of an axial force. The writer has tried this and found it did so. This shows that an axial force exists with solid conductors and that it is not necessary to resort to hydraulics to explain the known results. Other experimental demonstrations could also be given, one of which is based on the well-known Ampere trough experiment. But physicists who limit themselves to the older ideas will no doubt again try desperately hard to put the older laws through other acrobatic contortions to endeavor to force them to fit the case, instead of gracefully admitting that these new forces may exist and helping to investigate them.

The writer believes it can be shown that there is a broad, general law, which corresponds with a similar general mechanical principle and which applies to all electric circuits, that will justify all these various new and old motions, as also any others that may yet be discovered. This will be discussed elsewhere. Briefly it is, that a current carrying circuit will, as in mechanics, tend to produce a n y kind of a motion which will diminish the potential energy of the system, which seems to mean any motion which will generate a counter e.m.f. This would include all the observed motions, whether perpendicular, lengthwise, inclined (corner effect or motor effect), self-crushing (pinch effect), self-elongation (stretch effect), as also continuous motions which do not change the ultimate size and shape of the circuit. All of these generate a counter e.m.f. and reduce the potential energy of the circuit.

Direct experiments in this field of high current density phenomena, to study these various forces individually, are tedious and difficult, as so many foreign factors are likely to enter to mask the results. Most of these forces probably increase with the square of the current, and may therefore not be very evident until the currents become very large.

The complete explanation of such movements as those observed in Fig. 3 may perhaps be somewhat complicated; the pressures due to the pinch effect are likely to be different in the neighboring resistors; the currents turn another corner at each of the solid electrodes, which were vertical and of iron, which is magnetic; the intensity of the flux changes very abruptly where the resistors join the bath; it seems not impossible that even the obscure Hall effect may become formidable at these high current densities. It is not safe to draw hasty conclusions in this new field of high-current densities under such involved conditions.

DISCUSSION.

G. H. Clamer[1]: The last sentence of the second paragraph on page 316 of Dr. Hering's paper is as follows:

"Many of these pinch effect furnaces are now in daily use." If Dr. Hering refers in this statement to the furnace now known as the Ajax-Wyatt Furnace, in which the pinch force is co-existing with motor force, his statement as to its wide use is true. Approximately one hundred of such furnaces are in daily use, and nearly one hundred additional contracted for.

In connection with this furnace mention should be made of the invention of Schneider[2], past president of the British Iron and Steel Institute, also president of the great Creusot Steel Works of France, who took out what I consider the basic patent covering an induction furnace having a liquid resistor outside of the bath, and by which heating of the bath and circulation are secured. Important also is the invention of James Wyatt, which I believe was responsible for the ultimate success of a furnace of the general Schneider form. It is true that pinch pressure is a co-existing force and is utilized in the Wyatt type due to the proportion of current to the cross section required. This was fully pointed out by Dr. Northrup[3] and myself[4].

In the paper by Dr. Northrup referred to, there is a mathemat-

[1] President, Ajax Electrothermic Corp., Trenton, N. J.
[2] Engineering (London), June 12, 1908, pp. 776-777.
[3] Journal, Franklin Institute, December, 1920.
[4] *Ibid* October, 1920. Also American Institute of Metals, September, 1917.

ical discussion of the forces existing in a commercial furnace of the Ajax-Wyatt type. Quantitative formulæ have been worked out by him. He states that it is reasonable to suppose that the two effects are in approximately the same ratio as the two forces which produce these effects. Also both the motor effect and internal pressure effect (pinch effect) increase with the square of the current. Therefore any increase in current will cause these two effects to increase in the same ratio.

On page 317 Dr. Hering refers to a double hearth form of furnace, and he has shown diagrammatically in his paper as Fig. 1, a form of resistor closely resembling that used in the Wyatt furnace. I find no such figure as this in the Hering patent referred to.

An important feature of the Wyatt furnace is passage of unlike currents through a resistor connected with a single pool about an acute angle in the resistor, but distant from the pool whereby the electrode difficulties are avoided, and in connection with this the provision made for preventing the choking of the stream of metal as it is ejected towards the crucible. This last is accomplished by eliminating the angles at the points where the resistor enters the bath. By this construction is secured maximum pressure at the lower point of the resistor and minimum pressure where the metal enters the bath. No provision for preventing the choking of the metal flow was made in the experimental furnace of Hering[5].

On page 319 Dr. Hering refers to an odd high-current-density phenomenon he noticed when passing a strong current through an open channel of mercury, which turned a right-angled corner. This he refers to as the "corner effect" and is illustrated in Fig. 2. This he states was rebaptized by me, who gave it the name of "motor effect," which he considers a misnomer. Surely the term "motor effect" is far more descriptive than "corner effect." Furthermore this descriptive term was not invented by either the writer or by Mr. Wyatt, as it was used in a text-book in 1911, and perhaps earlier[6].

Wyatt first described his invention in a memorandum to which drawings were attached describing the invention of what is now

[5] Patent 1,162,773.

[6] Electric Furnaces in the Iron and Steel Industry. Rodenhauser-Schoenawa-Vom Baur, 1917, 2nd Ed., p. 39.

known as the Ajax-Wyatt furnace. In this description of the furnace, witnessed by signature of both the writer and Dr. Hering, he states that he does not positively explain the nature of the force, but believes it results from the following:

(1) Pinch effect as described by Hering, Northrup and Barry.

(2) Motor effect, which is caused by the repulsive action of two conductors carrying unlike currents, thus causing the particles of metal in the conductors to be repulsed as far away from each other as possible.

(3) Thermal effect.

All subsequent investigations thus far made have proved the correctness of Wyatt's assumption. He did not invent the "motor effect" any more than Dr. Hering invented the "pinch effect." Each of these inventors made observations that these forces were manifesting themselves under conditions existing in the experiments they were conducting. The observations were made possible by reason of accidental conditions. Dr. Hering afterwards made use of the knowledge resulting from his accidental observation and the scientific explanation of Dr. Northrup explaining the phenomenon, in the construction of an electrode furnace that depended for its operation upon this force. Likewise Wyatt made use of the knowledge gained in his observation of electrode furnace construction for producing a novel and successful induction furnace. Dr. Hering's 1907 paper concerning "pinch effect" preceded his patent application by more than two years.

For the same reason that Dr. Hering's 1907 discussion of the effect of pinch in electric furnace work formed no bar to the issue of his pinch patent, No. 988,936, using the pinch advantageously, so the showing of a motor effect in the early structures of Dr. Hering's patents presented no obstacle to the different application of motor effect by Wyatt in cooperation with pinch effect in his successful furnace. In the Hering patent, process claims are included so that so far as the application of the process is concerned, it may apply to either type of furnace, namely, electrode or induction. The inventions of these two men are, I feel, entirely distinct and radically different in kind.

Schneider was the inventor of the closed molten metal induction furnace having a hydrostatic pressure upon the resistor. In the

Schneider furnace, as constructed and operated by him in France, some "pinch pressure" was naturally present. This, however, was not recognized or usefully applied by him. Pinch pressure is naturally a matter of degree, depending upon the relation of magnitude of current to dimensions. The Hering method if used alone in an induction furnace, without co-operative motor effect also, is an improvement upon the original Schneider furnace.

I believe it is perfectly feasible to make a furnace of the induction type in which pinch pressure only, without motor effect, is used. I am not so certain, however, that such a furnace could be used in melting yellow brass that contains a high proportion of volatile metal, namely, zinc. I know of no commercially successful furnace of that type that has as yet been made. In the Wyatt furnace is secured not only the advantage of the improvement over the Schneider furnace, that should be attributed to Hering, but also the additional advantage of "motor force" that makes it possible to build a furnace having not only a very high power factor, but also permitting of a decidedly practical and simple construction.

Wyatt combined the pinch effect and motor effect in a furnace having the resistor under hydraulic head which had been invented by Schneider, obtaining flow in both directions in each of the branches of the resistor channel as distinguished from use of pinch effect only in the original Hering patent, and the uni-directional flow due to motor effect, in his so-called "W" patent. Uni-directional flow requires that the motor effect shall overcome and reverse the pinch effect in one branch of the channel. Each of these inventors, therefore, I believe had a different object and result, in the use of the pinch and motor effect and in the directions of hydraulic flow.

At the bottom of page 319 Dr. Hering refers to a curious effect of two currents making an angle with each other. This fact was made use of in the so-called "W" furnace as mentioned in Fig. 3. Such a furnace, as he has stated, was exhibited before this Society at Niagara Falls in 1914.

The object sought in applying the curious effects referred to was to get, as he has stated, the much desired uni-directional flow through the resistors. The whole specification and the patent

covering this furnace referred to in foot-note 11, bottom of page 321, is directed to this feature. No such flow exists in the Wyatt furnace. The flow is from the acute angle outwardly into the bath along the side of the leg of the resistor furthest from its neighboring leg, and inwardly along the adjoining sides of the respective resistor legs. Namely, the flow is inward and outward from the acute angle and is not at all uni-directional as in the construction shown by Dr. Hering. The current in Dr. Hering's construction flows from the electrodes in parallel through the resistor legs, and it flows through the legs of the resistor in the Wyatt furnace in series.

Carl Hering: My paper dealt with technical matters only, and it was not intended to bring up any patent matters. The bulk of Mr. Clamer's discussion is therefore unwarranted and entirely out of place. The patent question which he raised is answered completely by the fact that the number of my patent mentioned in the paper is on the name-plate of all of the Ajax-Wyatt furnaces which have been sold. As for what is shown in that patent, I do not think that need be discussed here, as anybody who is interested can consult the patent itself. Work on the furnace shown in Fig. 1 was stopped, but decidedly not on the ground that it was a failure. The resistor in that particular double-hearth furnace was of course below the level of the liquid and is so shown in the patent. Therefore, Mr. Clamer is mistaken also in that feature regarding it. I think that is all that needs to be answered, as the rest of Mr. Clamer's discussion is out of place here.

Henry Hess[7]: I want to take issue with Dr. Hering in one statement he makes. He referred to a rail through which a very heavy current passed being buckled; he also refers to the fact that the passage of currents creates a longitudinal—what one would call tensile force. Now it is a well-known thing to every mechanical engineer that a tensile force impressed on any tension member will straighten that member and not buckle it. I think that my understanding of the statement must be in error in some way.

[7] Philadelphia, Pa.

Carl Hering: Replying to the statement of Mr. Hess, if a long helical spring is very much compressed and only the ends are secured, it will tend to buckle, forming a figure something like the letter "S," by trying to lengthen itself; this, in my opinion, is just exactly what an electric circuit will tend to do; it tends to stretch itself, and if given an opportunity to move sideways, it will do so to get longer. It is therefore a little different from a tensile force, it is a stretching force, a tendency to grow longer.

W. S. Landis: I think what it amounts to is whether tensile strength has positive or negative sign.

A. G. Betts[8] (*Communicated*): In the furnace outline, given in the Fig. 3, page 318, the electric current at the angle at the center openings can be considered resolved into components, as

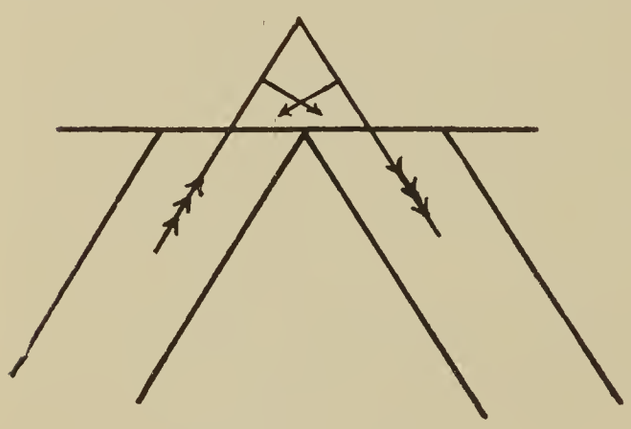


Fig. 1

Fig. 2

shown in my Fig. 1, or treated as having a substantially circular path, as shown in my Fig. 2. If a magnetic field having vertical lines of force, or lines of force having a vertical component, is established at this corner by the current itself, or otherwise, then the conductor will have impressed on it a mechanical force in the direction of the arrows (or the reverse according to the polarity of the field). If the magnetic field is reversed with each reversal of the current, the mechanical force will always have the same direction. Dr. Hering does not state whether he intensified the magnetic field by the presence of iron.

That the type of furnaces mentioned was not original with Dr. Hering can be noted by referring to U. S. Patent 816,554, April 3, 1906, showing mechanical, thermal and electromagnetic methods of maintaining circulation in the heating channels. Dr.

[8] Hot Springs, N. C.

Hering's electromagnetic pump in his Fig. 3 is simple as far as shown, but it would be interesting to know whether there are important details of construction or not.

CARL HERING (*Communicated*): When I replied briefly at the meeting to Mr. Clamer's long discussion, I assumed that his remarks would be ruled out of order, as was suggested on the floor by a member. As subsequently revised for publication, I desire to make the following brief reply:

The pinch-effect furnaces referred to by me as being in use have the numbers of my patents on their name-plates, as Mr. Clamer well knows; moreover he admits that the pinch effect is used in them. The old Schneider patents (now expired I believe) are for induction furnaces and do not describe the pinch effect, which was not yet known at that time. If Wyatt was "responsible for the ultimate success" of the Schneider induction form, it was because he added the pinch effect and corner effect. The reason I did not patent this particular combination separately during the early developments was because it was considered to be covered by my basic patents.

Mr. Clamer says he cannot find the double-hearth type with an acute angled V-shaped resistor (Fig. 1 in my paper) in my patent. He is mistaken; it is there and was reproduced in Met. and Chem. Eng., January 15, 1916, p. 100. Both the pinch effect and the corner effect are described in that patent as acting in that V-shaped resistor, and in the type shown they are combined together and operate identically as in the Wyatt form. Mr. Clamer is, therefore, mistaken in attributing this to Wyatt; he tries to divert attention to another patent in which another effect was desired. Mr. Clamer should have consulted these published descriptions before making such misleading statements in public before a scientific society. I have given many references to published descriptions, so that anyone interested can look them up. In addition there are some further signed, dated and witnessed early disclosures which have not yet been published.

Means for preventing the so-called "choking" of the metal flow, which is not a serious matter, were shown in my very first patent, and were used. It is important to note that Mr. Clamer does not deny that my early description of the "corner effect," referred to in this paper, was long prior to Wyatt's application of it. In the

reference which he gives to the old use of the term "motor effect" in 1911, it will be seen that it was then used to describe the pinch effect; no other kind of motor effect is described in that early reference. The Wyatt "memorandum" does not claim the corner effect as original, as would seem to be implied by Mr. Clamer's transcript of it; he omitted to state that this "memorandum" was dated long after my patents in which all these forces were described.

Replying to the communicated discussion of Mr. Betts, the magnetic fields were not intensified by the presence of iron or magnets in any of the commercial forms of the furnace, as the pinch effect alone is quite strong enough; it tends to be too strong rather than too weak. But the effects of superimposed magnets and iron were experimented with, as stated in the last paragraph on page 315; they have a very pronounced effect on these self-produced or internal forces. His patent to which he refers contains no reference to the pinch effect or to any of these other new forces, or to any forces like them; the pinch effect was not yet publicly known when his patent was applied for in 1904. The only electromagnetic forces mentioned in it are the older ones known to Ampere and Oersted. I, therefore, do not see how it can in the least affect the originality, as I never made any claims to have been the first to produce circulation in a furnace, nor does the Betts patent describe any of these new forces. Replying to his last sentence, there are no essential details of construction other than proper proportioning and having the depth of metal over the resistors sufficient to prevent the snorting referred to. But, of course, there are many details of construction which improve it as a commercial furnace.

In my paper, I said that a more detailed discussion of these new forces from the standpoint of physics would appear in another paper; this has since been published in the Journal of the Franklin Institute for November, 1921, under the title of "Revisions of Some of the Electromagnetic Laws." The feature of possible interest to the electric furnace engineer is that a revision of some of our older laws seems now necessary in my opinion and if this is correct, the doors which have been closed to us by some of our former laws and have stopped progress, are now opened, making developments possible in entirely new fields.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 22, 1921, President Landis in the Chair.

RECENT PROGRESS IN HIGH FREQUENCY INDUCTIVE HEATING.[1]

By E. F. Northrup.[2]

Abstract.

A description of the present status of high-frequency oscillating current furnaces for experimental, laboratory and commercial work. Also of the high-frequency converter sets made for use with them. Furnaces of seven types are described in detail and the actual performances given, showing them to run at 30 to 40 percent electro-thermal efficiency. The largest furnace described takes 60 kw. and can melt 600 lb. (275 kg.) of silver.—[J. W. R.]

At the general meeting, at New York City, April 3, 4 and 5, 1919, the writer presented a paper before this Society entitled "Principles of Inductive Heating with High-Frequency Currents." The concluding paragraph of this paper reads, "The presentation given above relates only to the basic principles which underlie this new method of electric heating, and no attempt has been made to give data and results of tests upon the performance of specific apparatus. A paper on this subject should follow later as the result of an engineering development which it is hoped the near future will see." It is the object of this paper to present in broad outline the progress which has been made in this engineering development in the two years just past.

Until April 28, 1920, the manufacturing of experimental and commercial apparatus pertaining to high-frequency inductive heating was carried on by the Pyrolectric Instrument Company, which company the writer organized. At this time the Ajax Electrothermic Corporation, with Mr. G. H. Clamer president, and the

[1] Manuscript received March 5, 1921.
[2] Vice-Pres. and Technical Adviser, Ajax Electrothermic Corp., Trenton, N. J.

writer vice-president, was organized. This company controls, manufactures, and sells the Ajax-Northrup High-Frequency Inductive Furnaces, and all methods of heating, covered by its patents, with high-frequency currents.

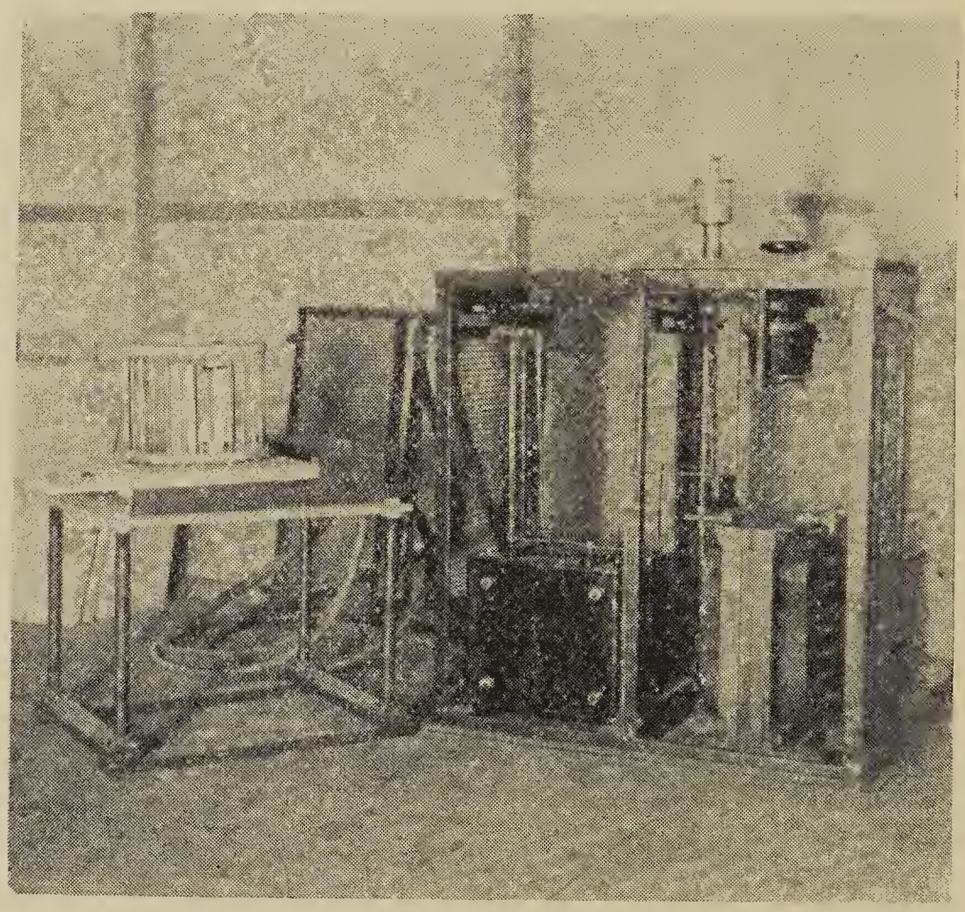


Fig. 1. Picture of 2 KW. H. F. C. Set.

HIGH-FREQUENCY CONVERTERS.

The high-frequency converter sets used for changing currents of commercial frequency into high-frequency current have been greatly simplified, standardized and perfected into thoroughly reliable static apparatus adapted for continuous commercial service.

Figures 1, 2 and 3 show respectively a 2, a 20, and a 60 kilowatt set.

High frequency converter sets rated under 25 kw. are designed for operation on a singe phase circuit, or on one leg of a polyphase circuit. A 60 kw. set (the largest so far constructed) is designed for operation on a three-phase circuit. It has been found advisable to use three-phase in place of two-phase when polyphase operation is desired.

These high-frequency converter sets embody three essential parts; an oil-cooled transformer, constructed with internal reactance, a set of static condensers, and a metal discharge gap. These essential parts are housed in a grounded metal cage. This

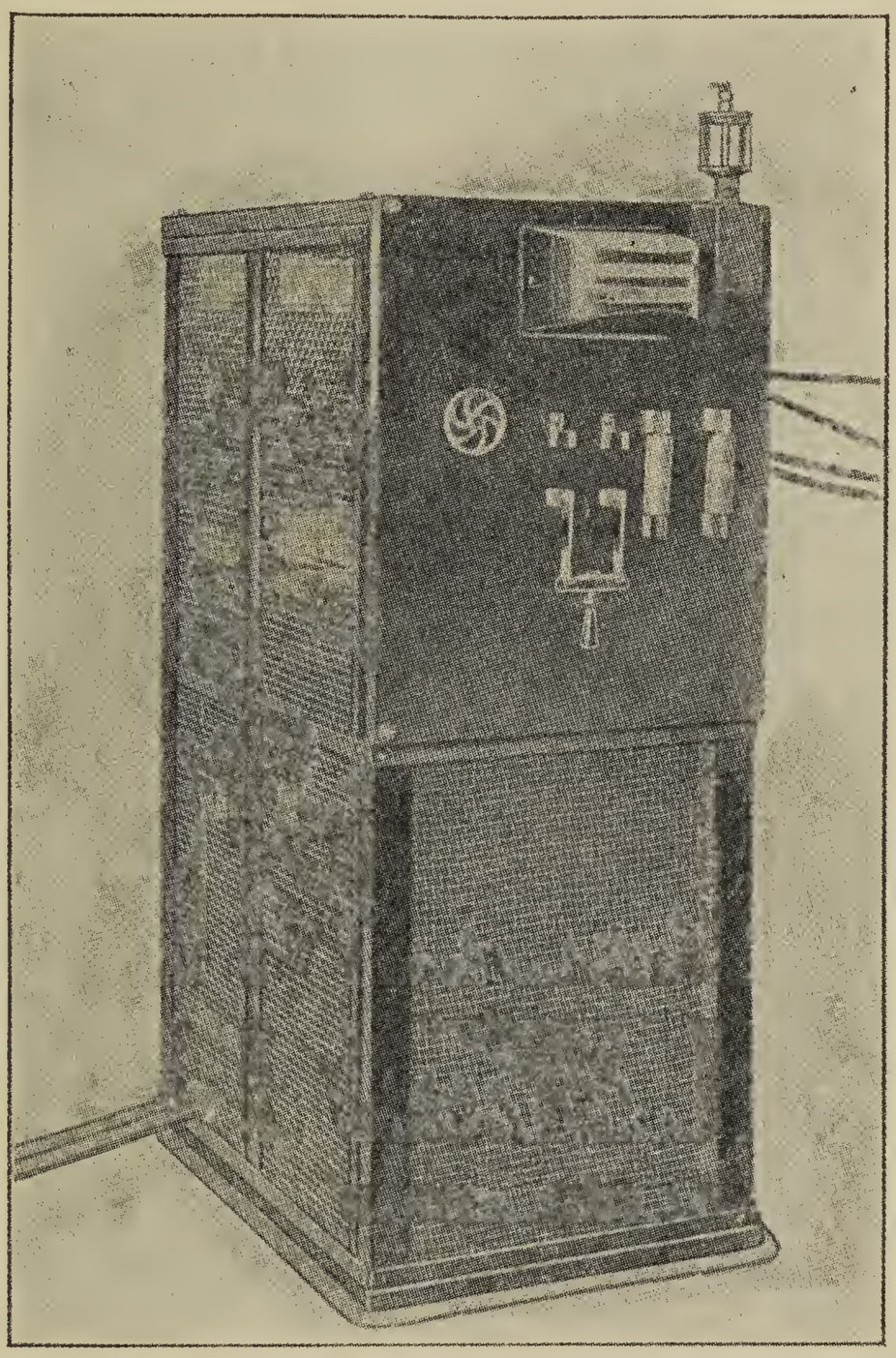


Fig. 2. Picture of 20 KW. H. F. C. Set.

cage is faced with a switchboard which has mounted upon it one double-pole starting switch, an alcohol dropper, and an indicating, or, in the case of three-phase operation, an integrating wattmeter. A round handle also appears on the face of the switchboard the

purpose of which is to control the power (by raising and lowering the electrodes of the discharge gap) by infinitesimal steps from zero to a maximum. The turning of this handle to get the power

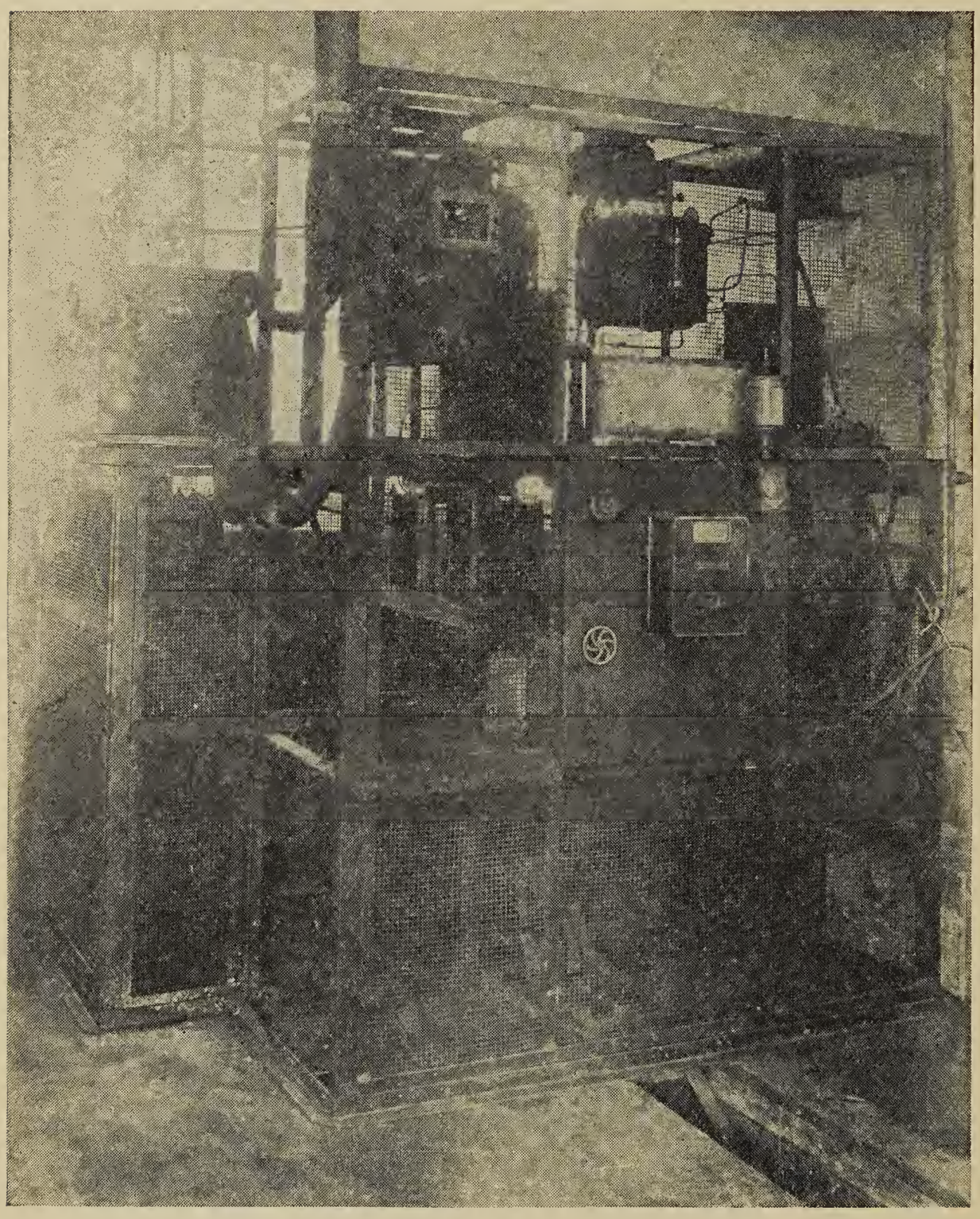


Fig. 3. Picture of 60 KW. Three-phase H. F. C. Set.

desired and an adjustment of the alcohol dropper when starting and stopping, is all the manual operation that is required for operating the high-frequency converter set.

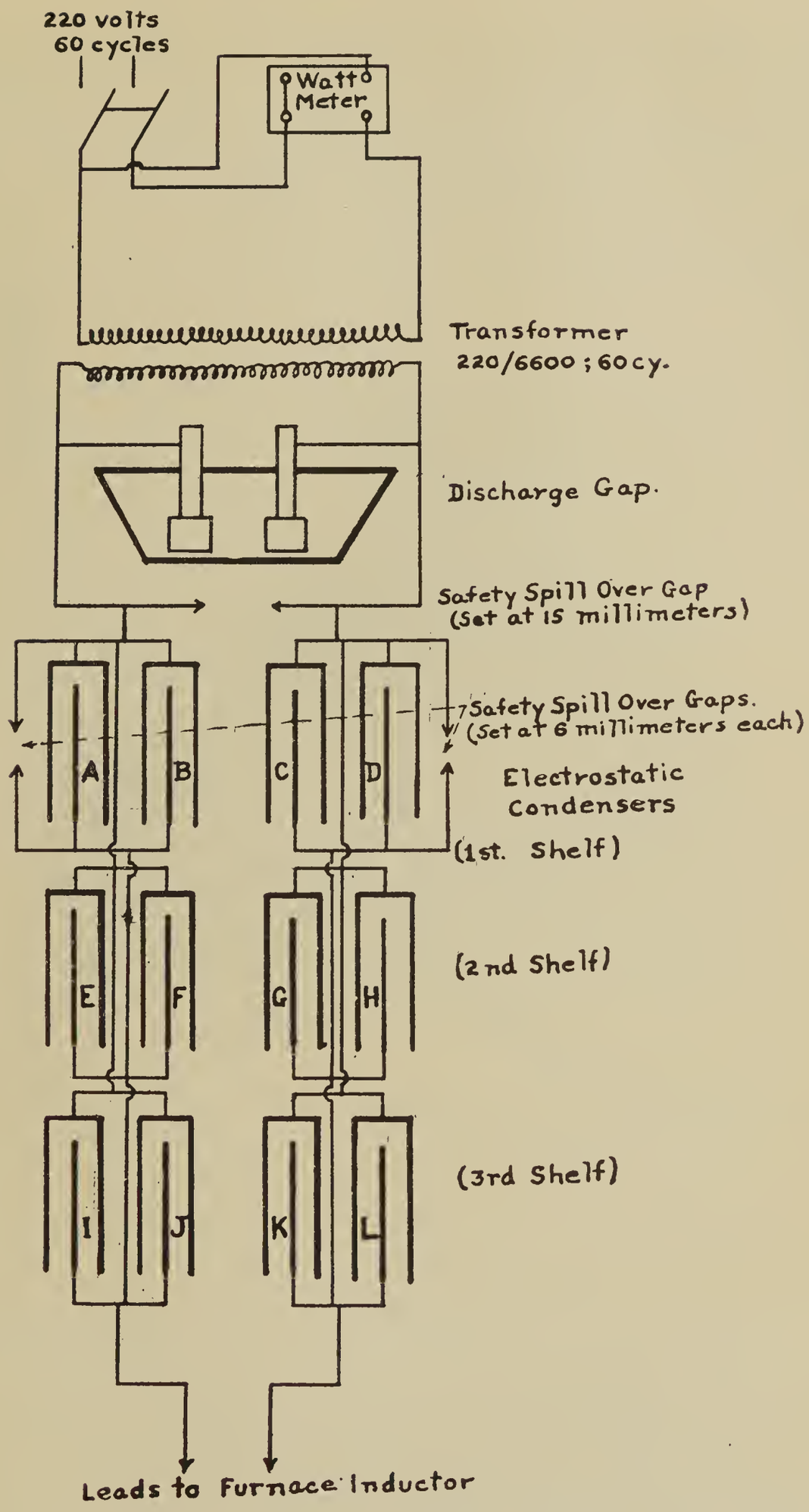


FIG. 4. Theoretical Diagram of Connections of 20 KW. H. F. C. Set.

The condensers used are manufactured by the General Electric Company. All high-frequency converter sets of whatever capacity make use of condenser units of the same style and

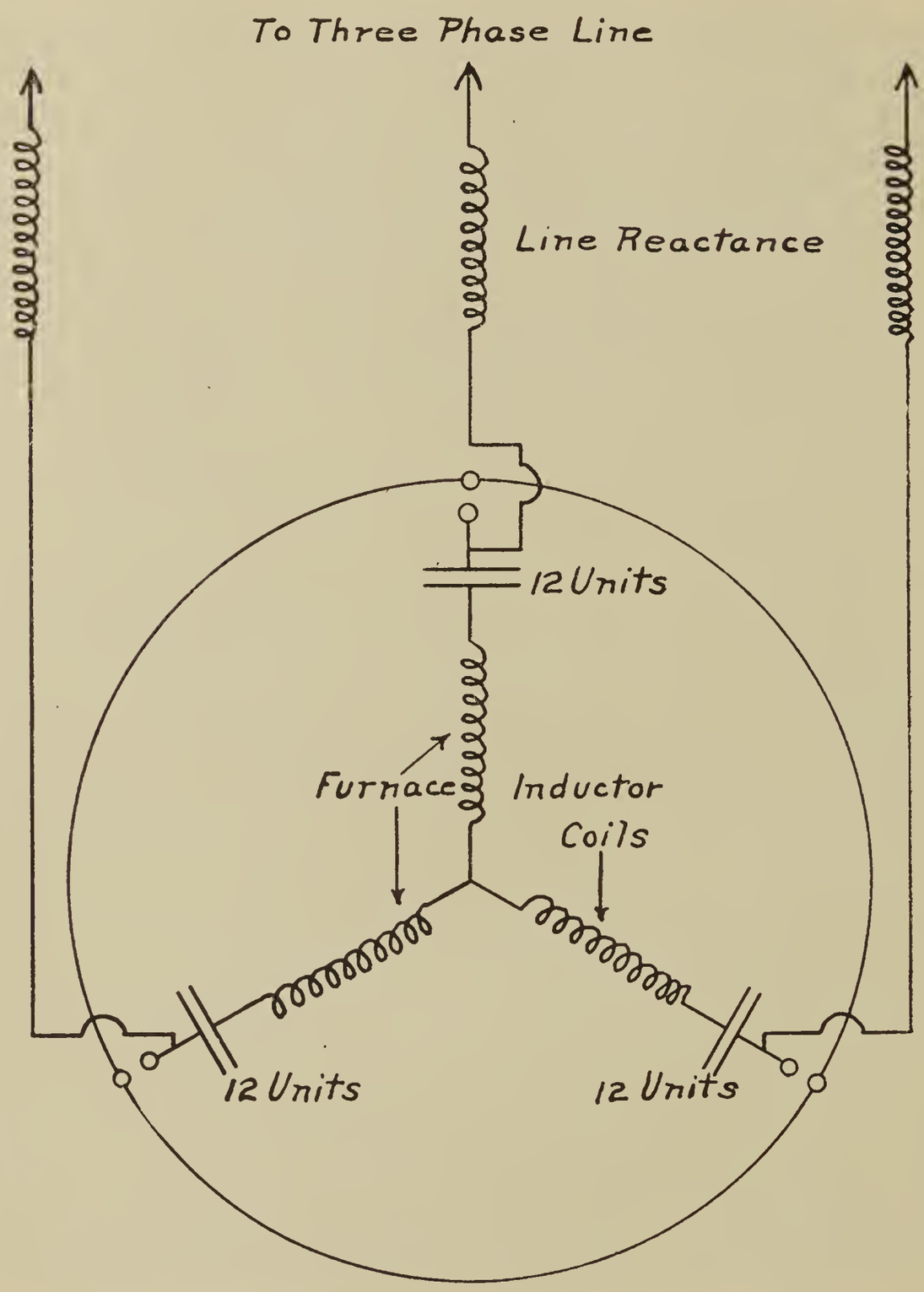


Fig. 5. Theoretical Circuits of Three-phase 60 KW. Set, Using Step-up Transformer.

rating. The number of units employed is about proportional to the kilowatt rating of the set. A 20 kw. set employs twelve units. Six of these units are joined in parallel on one side of the oscillating circuit and six on the other side.

The circuits of a 20 kw. high-frequency converter set are given in Figure 4.

It should be noted that the high-frequency oscillating circuit through the inductor coil of the furnace is entirely separated by the two sets of condensers from the low-frequency high-tension circuits. As high-frequency current will not draw an arc nor cause severe shock, this arrangement insures safety to the furnace operator.

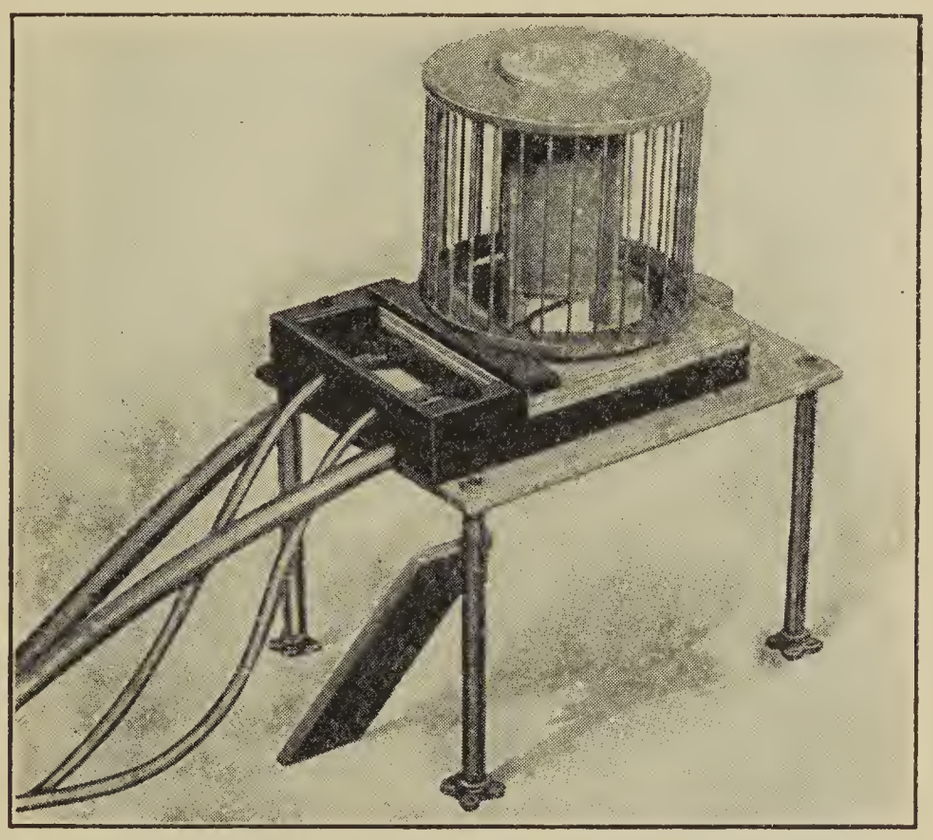


Fig. 6. Standard D-1 Model Furnace.

The circuits of a 60 kw. set designed for operation with three step-up transformers on a three-phase circuit are given in Figure 5. The set employs thirty-six condenser units.

Though a large number of General Electric Company's condensers are in service, some having been used for over a year in hard commercial work, not one unit has failed through rupture or over-heating.

A 20 kw. high-frequency converter set occupies a floor space of 29 inches (73 cm.) front by 41 inches (103 cm.) deep, and stands 67 inches (1.68 m.) high. A 60 kw. set occupies a floor space of 81 inches (2 m.) front by 41 inches (103 cm.) deep, and

stands 67 inches (1.68 m.) high. In cases where the supply voltage is 6,600 volts it is practicable to operate the three-phase high-frequency converter set directly off the supply circuits, no step-up transformers being required. On the other hand, three high-tension reactances of 25 K. V. A. capacity must be inserted in the supply line to limit the flow of current. An oil-switch must be used as a starting switch; two current and two potential transformers are needed to operate the integrating wattmeter. There

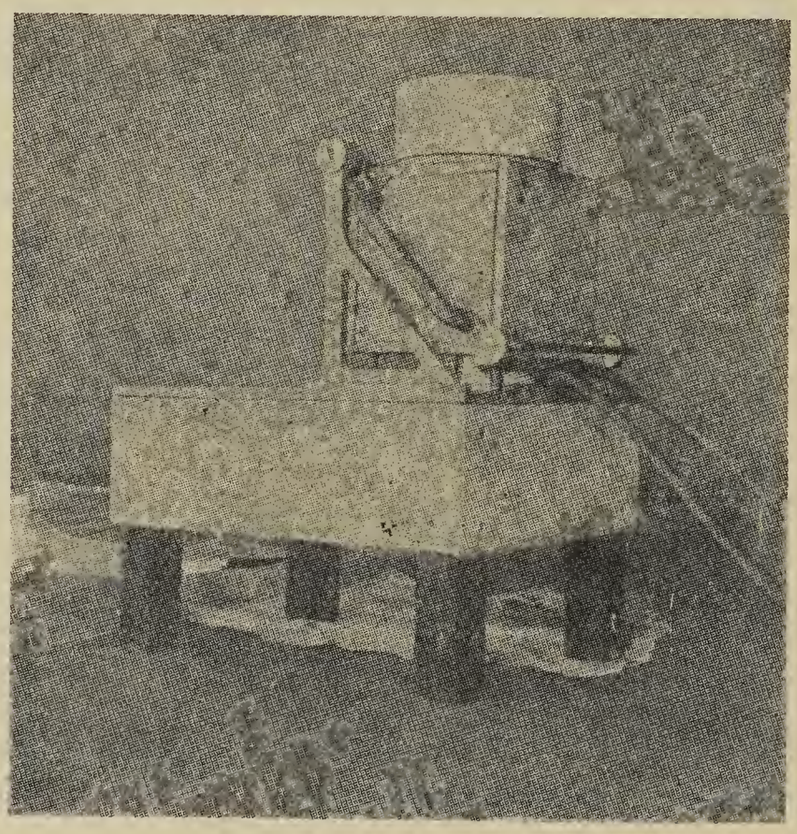


Fig. 7. Six-inch "Electric Crucible."

is, therefore, a loss in simplicity and little is gained in economy of first cost in operating directly off high-tension supply lines.

On account of the intrinsic high cost of transformers and condensers, these high-frequency converter sets constitute from eighty to ninety percent of the selling price of a complete metal melting outfit. The high-frequency converter sets have, however, no moving parts and the nature of the materials which enter into their construction is such that they depreciate scarcely at all.

These high-frequency converter sets have proved in practice to be so reliable and efficient, as constructed in units not exceeding 60 kw., that a high-frequency alternator of this rating could

scarcely compete with them in simplicity, ease of operation, life and cost. It is only when we have single units of over 100 kw. capacity to consider that we should look to the high-frequency alternator, of about 12,000 cycles per second, as the better apparatus for supplying high-frequency current for heating purposes. Satisfactory alternators of 200 kw. capacity have been designed, but as yet none such has become available.

MELTING FURNACES.

Furnaces for melting practically all metals, and also glass and refractories, have been designed, built and sold.

These furnaces, any of which may be operated by one of the above high-frequency converter sets, divide into seven classes:

(a) High temperatures and vacuum type furnaces.
(b) "Electric crucible" type furnaces.
(c) Mint type furnaces.
(d) Heat treatment furnaces.
(e) Graphitization furnaces.
(f) Miscellaneous heating and muffle type furnaces.
(g) Large tilting and pouring-type furnaces.

It is obvious that if the available power is limited to a definite maximum, the highest temperature can be obtained only by restricting the volume of the mass to be heated.

(a) High Temperature and Vacuum Furnace.

The highest temperatures may be obtained with a furnace energized with a standard 20 kw. high-frequency converter set when patterned after the standard high-temperature furnace shown in Fig. 6.

The inductor coil of this furnace is made of forty-two turns of ⅜ inch (1 cm.) flattened copper tubing. The inductor is wound as a solenoid and is 9 inches (23 cm.) long and 4 3-16 inches (10.5 cm.) in inside diameter. The high frequency potential is applied to the terminals of this solenoid and also a water pressure of thirty pounds (13.7 kg.) or more, which maintains a flow of water through the flattened tubular solenoid. The furnace may be used as a vacuum or as a non-vacuum furnace. It is of the non-tilting type, and its contents are removed through the

bottom by withdrawing a slide of asbestos board. This type of furnace under favorable conditions will melt molybdenum and can be used to melt electrolytic iron in five to six pound (2.3 to 2.7 kg.) lots strictly carbon free. The furnace is very suitable for the recovery of platinum scrap. When a crucible of carbon or Acheson graphite 2¼ inches (5.6 cm.) inside diameter by 7 inches (17.5 cm.) long is used, and this is heat-insulated with lampblack, it is not difficult to obtain temperatures in from fifteen to twenty minutes which are more than sufficient to completely graphitize carbon.

For melting in vacuum, a quartz tube closed at the bottom is used which just fits the coil. This tube is fitted at the top with a water-cooled cover with a connection for exhausting the air. Refractories insulate better under high vacuum conditions, and the highest temperatures are easily obtained in vacuum with an expenditure of ten or fifteen kilowatts.

(b) "Electric Crucible" Furnaces.

This type of furnace has been constructed in four sizes. The inductor coil and crucible are conical. The furnace sits upon a low table and makes contact with the high-frequency converter terminals by means of two metallic feet.

All furnaces of this type are designed for pouring the metal contents in the same manner in which the contents of an ordinary crucible are poured, over its edge; hence the term "Electric Crucible." An "Electric Crucible" may be lifted by handles, placed on two opposite sides, entirely off the table and poured; or it may be pivoted, around an axis passing through its pouring spout, on trunnions. In this case it is lifted by a handle on the side in the back, and poured. Figure 7 is a view of a 6 inch (15 cm.) "Electric Crucible."

This one can either be tilted around the axis supported by trunnions, or it may be lifted by the handles on its side, entirely off the table, and poured. If it is remembered that all types of furnaces operated by high frequency induction are substantially at room temperature on the outside, the practicability of handling a furnace in these ways is readily seen.

This particular style and size of furnace is well adapted to melting precious metals, especially gold and platinum alloys. The

furnace will melt and pour about ten to fifteen pounds (4.5 to 6.8 kg.) of copper, or about eight to ten pounds (3.4 to 4.5 kg.) of steel. The melting is extremely rapid, and when non-conducting crucibles are used, as would be the case when melting a platinum-gold alloy or a ferrous metal, the molten metal stirs violently—a circumstance which assures the perfect mix of an alloy.

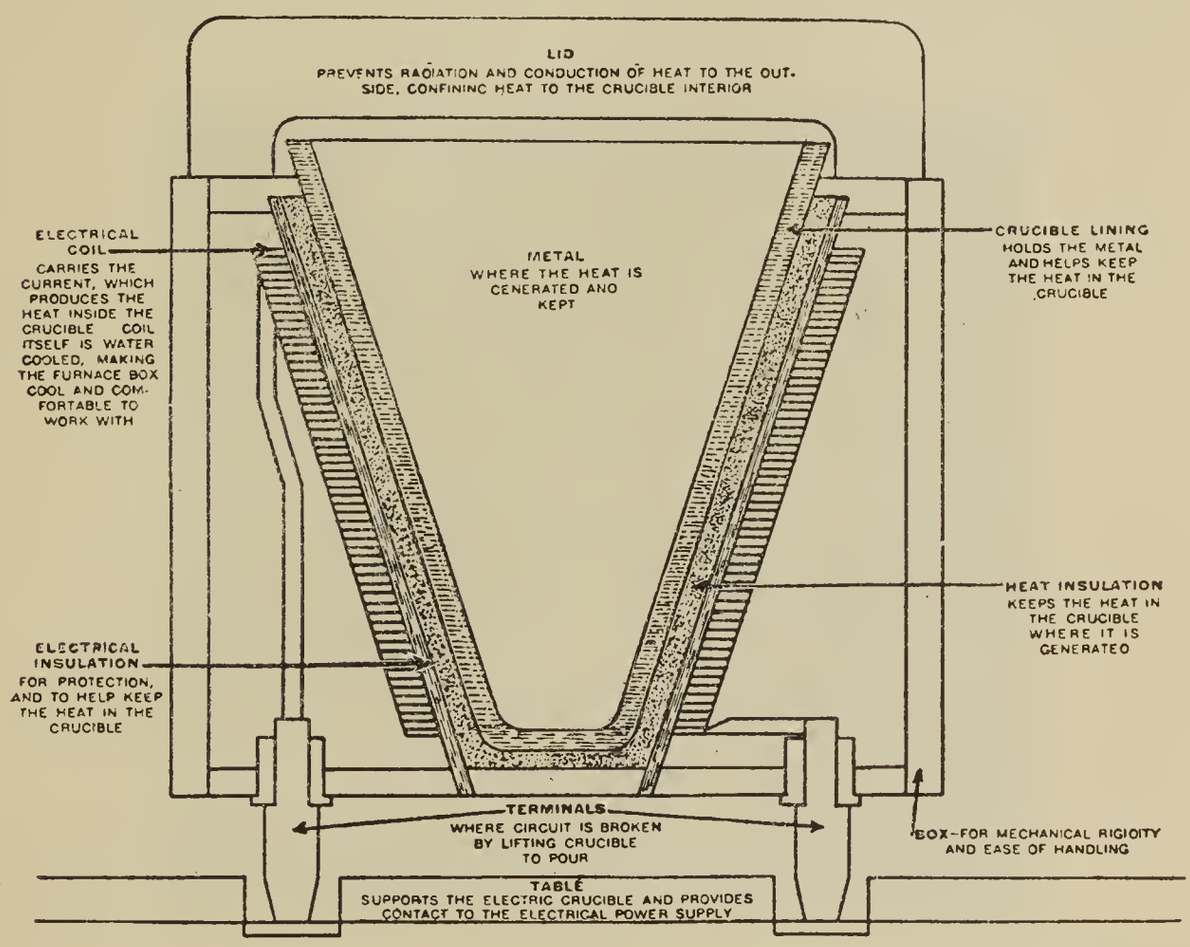


FIG. 8. Cross Section of Ten-inch "Electric Crucible."

Figure 8 is a cross-sectional view of an "Electric Crucible" in which the crucible is about 10 inches (25 cm.) in diameter at its top. It is designed to hold and melt about fifty pounds (22.7 kg.) of copper or brass and about twenty-five pounds (11.4 kg.) of steel. In this case a pour is made by lifting the "Electric Crucible" clear off the table on which it rests. The crucible is lifted and tilted for pouring by two persons, using detachable handles.

Figure 9 shows the writer (on the right) and his assistant, Mr. Soden, pouring twenty pounds (9.1 kg) of chromium steel. This steel has been melted in a non-conducting crucible from steel

turnings, hence the carbon content of the steel has not been changed. It required 15 kw. and fifty-five minutes to make this melt, starting with the furnace cold.

For melting pure platinum and iridium free from all contamination, an "Electric Crucible" has been made with a conical crucible 5⅜ inches (13.4. cm.) in diameter at its top. This conical crucible is made of moulded silica ware. Fitting in this is the crucible proper, which holds the metal to be melted. This

Fig. 9. Pouring a Ten-inch "Electric Crucible."

crucible can be moulded of such suitable materials as lime, electrically shrunk magnesia, or the like. The purpose of the outside quartz crucible is to give perfect electrical insulation between the conical inductor coil and the metal contents of the crucible. The melting is, of course, produced by the currents which are generated by the inductor in the metal itself.

In using the above three "Electric Crucibles," in which it may be required to obtain very high temperatures, it has been found advantageous to maintain a flow of water through the inductor coil. The water connections to the coil are made with rubber tubing a meter or more long, and it has been found that the

resistance of this length of water column is sufficiently high to prevent the water circuit from acting as a shunt on the electric circuit.

A larger "Electric Crucible" without water connections and with a practically cylindrical crucible is, at the date of this writing, under construction. It is designed for melting and pouring brass or bronze in 200 pound (91 kg.) lots. To secure more

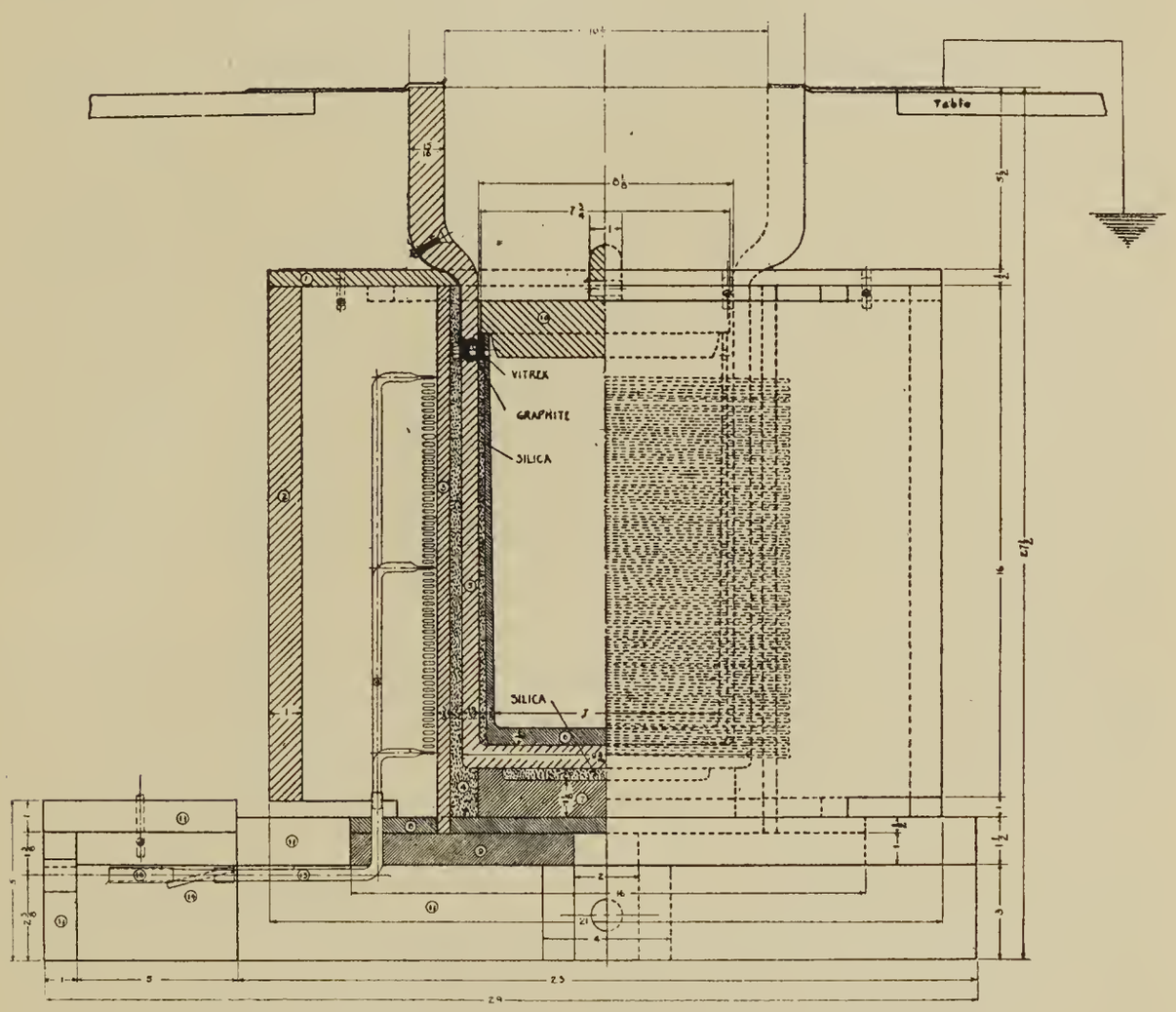


FIG. 10. Cross-sectional View of Small Mint Furnace.

rapid melting, a 25 kw. high frequency single-phase converter set will be used. As this type is a very recent development, performance data are not yet available.

In the 6 and 10 inch (15 and 25 cm.) "Electric Crucibles" copper melts and superheats to a suitable pouring temperature at the rate of about 4.2 pounds (1.9 kg.) per kilowatt hour. As will be shown later, the melting rate with larger furnaces and more power is very considerably increased, twenty-five percent or more.

(c) Mint Type Furnaces.

This type of furnace was designed specially for use at the United States Mint in Philadelphia, Pa., in connection with work carried on in the deposit melting room.

Four furnaces of the same general type have been installed at the Mint for over a year, and two of these "have been operating daily since March 20, 1920, on small deposits, two small crucibles being used to each furnace, which practice has been followed on combustion furnaces for years past."[3] The other two furnaces have more recently been put into continuous operation. "The results of a test run, melting fine silver bars, were as follows: Total amount melted, 13,478.50 ounces (382,115 gm.); total time consumed, seven hours; total current used, 156.50 kilowatt-hours; pounds melted per kilowatt-hour, 5.905 (2.68 kg.); average load per phase, 12½ kilowatts. The results will be greatly improved when the capacity of furnaces is reached by having a full quota of condensers (which are now being installed) using 16 kilowatts per phase instead of 12½. The fuel cost at the rate of consumption shown above compares favorably with gas."[3]

These furnaces are cylindrical, stationary furnaces and are designed for melting metals in a crucible which may be lifted out of the furnace and poured. In the larger furnaces the molten metal is dipped out until only a little remains in the bottom of the crucible. This last portion of metal is removed by then withdrawing the crucible and pouring it out. In the smaller furnaces the metal deposits are placed in small crucibles and lowered into a thin-walled graphite crucible within the furnace, which remains permanently in the furnace.

The four furnaces of this type installed at the Mint use a total of forty-eight kilowatts.

Figure 10 is a cross-sectional view of one of the two smaller furnaces which is used exclusively for melting down precious metal scrap in small crucibles.

In the 1920 Report of the Director of the Mint, on page 20, a very favorable comment is made on these furnaces and it is there stated that their adaptation to Mint work on precious metals is advantageous.

[3] Annual Reports Director of the Mint (1920), 19.

Furnace Crucibles—Coated Crucibles.

In high-frequency induction heating of ferrous metals and other metals of high resistivity, as platinum, non-conducting crucibles are used. In melting gold, silver, copper and other metals which do not tend to take up carbon at a high temperature it is better to employ a machined graphite crucible or a moulded carbon crucible.

The single objection to these crucibles has been due in the past to the rapidity with which they oxidize and burn away at high temperatures when exposed to the air.

To overcome this defect the writer made a research to find a coating which could be put upon graphite or carbon that would have the following properties:

(a) It must withstand a temperature of 2,000° C. at least.

(b) It must be impervious to air at this temperature, at least to the extent that the graphite shall not oxidize beneath the coating and cause it to scale off.

(c) The coating must have a chemical union with the carbon to make it cohere to the carbon tenaciously.

(d) It must be of a nature such that other coatings of the same or other material may be laid over it, and cling tightly. This second coating should be capable of selection such that molten metals, even steel, will not dissolve it.

These results have all been secured. A graphite crucible thus coated—sample of which is here shown—will not oxidize when it is at a temperature of 1,800° C. and a jet of oxygen is steadily blown upon it.

The foundation coating is put on at a temperature exceeding 2,200° C. An additional coating of zirkite, magnesite, etc., may easily be added as desired.

These coated crucibles are particularly useful in the "Electric Crucibles" which may be operated with the cover removed, and the coated crucible freely exposed to the air when hot. These coated crucibles, however, have been made too recently for working life tests with them. It is to be expected that they will have a prolonged life which will make the crucible cost for high-frequency induction furnaces very low.

(d) Heat Treatment Furnaces.

These cannot here be described further than to state that steel of any shape, even thin knife blades, or such commercial products as the cutting knives of lawnmowers, when placed in an inductor coil energized with current having a frequency of 20,000 cycles, is rapidly and uniformly heated to the proper quenching temperature. The heating in this case is due largely, and in the case of thin steel sheets almost wholly, to the development of heat by hysteresis loss in the magnetic material.

This type of furnace should have a wide commercial application, though up-to-date furnaces mostly have been constructed for merely demonstrating the principle; one, however, is in commercial operation at the plant of the Cleveland Twist Drill Co., for straightening twist drills.

(e) Graphitization Furnaces

The best of all heat insulators at temperatures above 2,000° C. is lampblack or carbon-black. It is also an electric insulator when not strongly compressed. Hence when a pile of carbon blocks are imbedded in this material and inductively heated with high frequency current, they are heated rapidly and uniformly, and can be quickly brought to the graphitization temperature. The efficiency compares very favorably with other methods.

Extensive tests have been made of this application of high-frequency inductive heating. These tests were made at the request of several of the leading manufacturers of carbon brushes and other carbon articles which require graphitization. The writer believes this commercial application of high-frequency inductive heating is deserving of special and immediate consideration.

(f) Miscellaneous Types of Furnaces.

There is no method of heating more versatile than high-frequency inductive heating, and there have been many demands on the manufacturers to supply furnaces of very special type, and for a wide variety of uses. We can only mention one example here. Figure 11 shows an annealing furnace for producing a temperature of about 1,000° C. uniformly distributed throughout a cylindrical chamber of 7 inch (17.5 cm.) inside diameter by 36 inches (90 cm.) long.

(g) Sixty Kilowatt Tilting and Pouring Furnace

A three-phase high frequency converter supplied with thirty-six condenser units will absorb 60 kw. from the supply line, and will deliver from 60 to 70 percent of this power to the terminals of a properly constructed furnace. Thus with 40 kw. actually supplied to the furnace, or as much as 35 kw. in the form of heat to the crucible itself, it is possible and desirable to heat crucibles

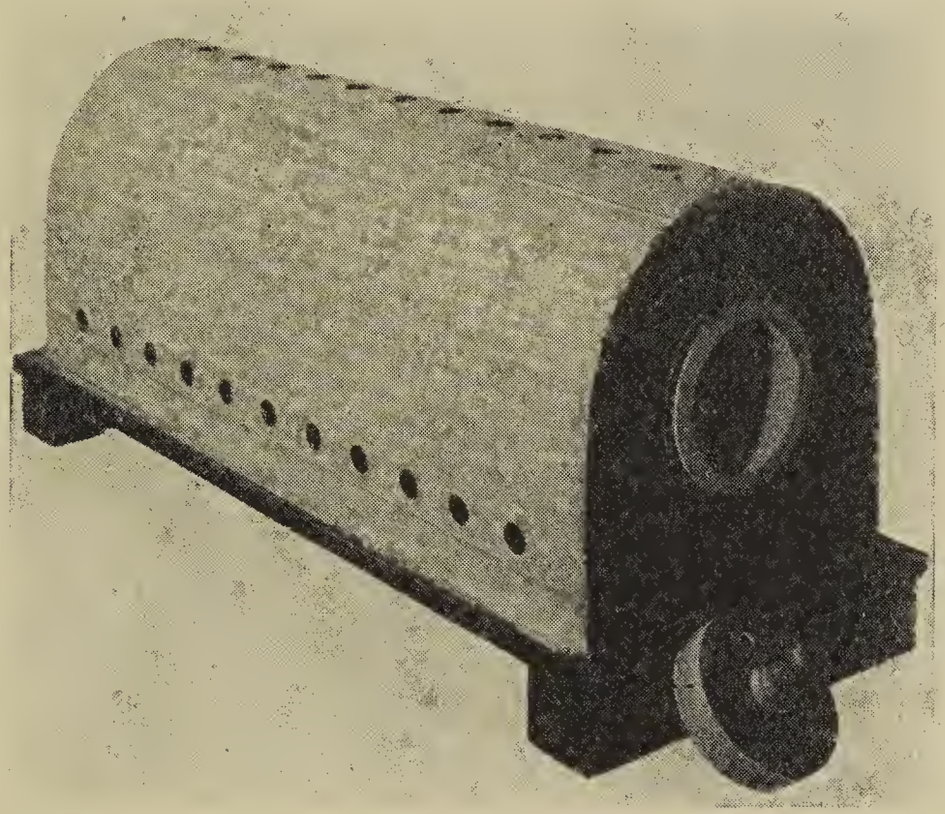


Fig. 11. Reproduction of Annealing Furnace.

which hold as much as 600 pounds (273 kg.) of silver, or equivalent weights of copper, brass, bronze or other non-ferrous metals which melt under say 1,200° C.

To handle and pour this quantity of metal it is advantageous to design the furnace for tilting and pouring through the medium of a heavily constructed mechanical mechanism.

One such furnace has been constructed, and is now in daily operation at the plant of Handy & Harman, Bridgeport, Conn. The furnace is designed and used for melting fine silver or sterling silver.

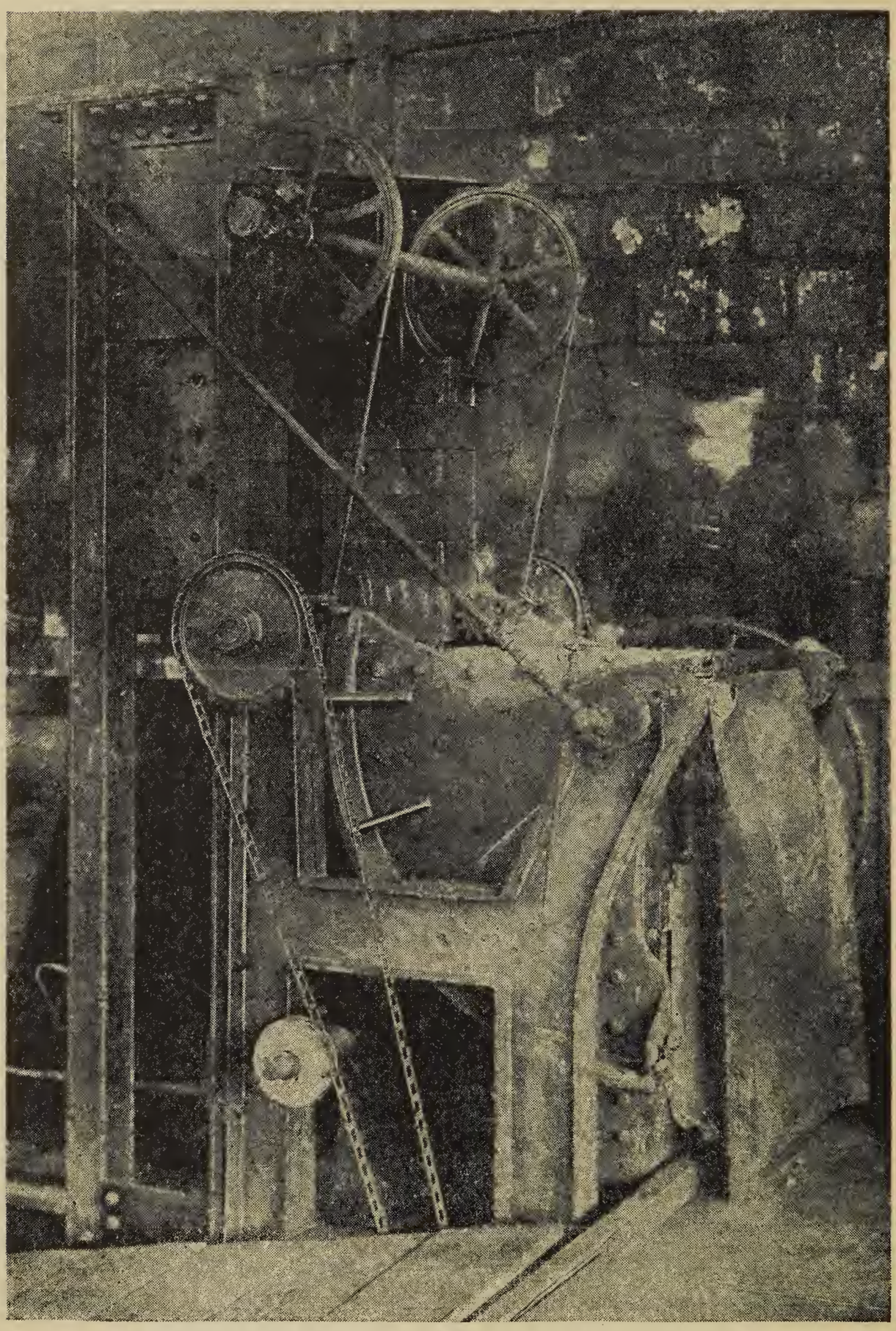


Fig. 12. Handy & Harman Furnace in Down Position.

The following features were embodied in its design and construction:

(a) The crucible and inductor coil are housed in a box made of sheet steel 5-16 inch (0.79 cm.) thick. The box is 45½ inches (114 cm.) high, 31¼ inches (78 cm.) wide, and 27⅝ inches (69 cm.) deep. The top of the box is fitted with a heavy moulded refractory piece. This has a central hole 10 inches (25 cm.) in diameter—the inside diameter of the crucible—and a carefully shaped pouring spout.

(b) The crucible and its steel housing may be rotated for pouring around an axis which passes exactly through the end of the pouring spout. The crucible may be raised in the process of pouring 15 degrees above the horizontal.

(c) The movable portion of the furnace is counter-weighted, whereby very little exertion is required to tilt and pour the charge.

(d) The space in front of the spout is free from mechanism, which permits moulds to be brought by a carrier directly beneath the end of the spout.

(e) The furnace is free for approach by a man or a truck from behind, which arrangement gives facility to the charging.

(f) The furnace when in its vertical position makes electrical contact with three leads from the high frequency converter, and when tilted for pouring breaks these contacts with no arcing. The furnace has, therefore, no moving electrical conductors.

(g) The inductor coils, three in number and star-connected, have water circulating through them. The water is led in and out of these coils at the two ends of the axis of rotation of the furnace, by which device all movable water connections are avoided.

(h) The inductor coils and the housing of the crucible and inductor coils are at all times at or near room temperature, which makes the furnace very comfortable to work around.

(i) The crucible is of carbon or Acheson graphite. It may be moulded or turned out of a section of 12 inch (30 cm.) Acheson graphite electrode.

The limits of this paper preclude a more detailed description here of this 60 kw. silver-melting furnace, but a very good idea

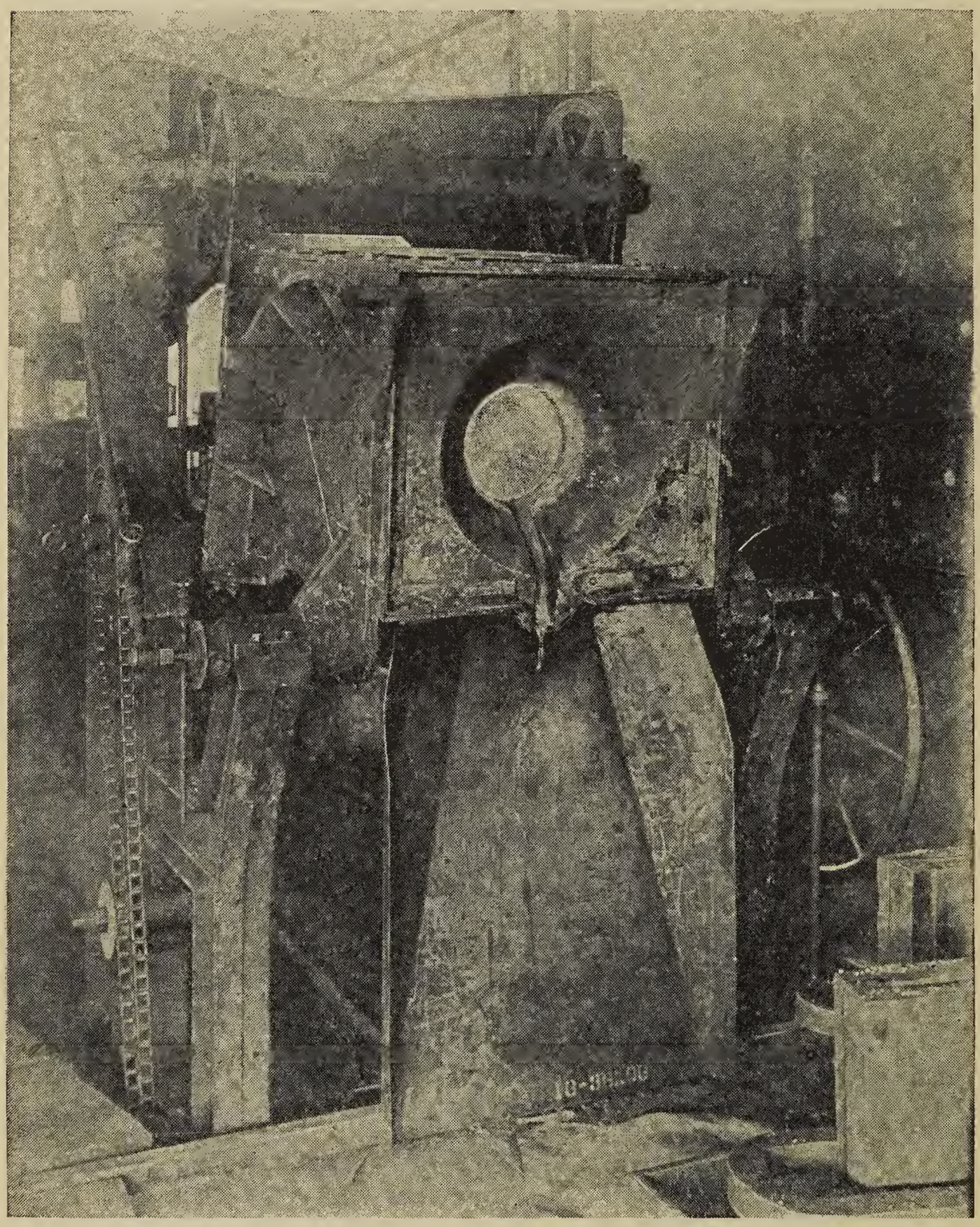


Fig. 13. Handy & Harman Furnace in Pouring Position.

may be had of the furnace and the three-phase 60 kw. high-frerial has been found suitable for many of the small furnaces that have been made.

(j) The electrical insulation between inductor coil and crucible is a cylinder of micanite of a 3/8 inch (1 cm.) wall (and thus is

TABLE I.

Report of One Day's Operation of Silver Melting Furnace.

Time	KWH. Meter	Current	KW.	Weight Sterling Silver Ounces	Notes
7.45	2727.3	8.5	..		
9.00	2759.0	8.5	53		Crucible at 961° C. Put silver in.
9.40	2796.5	8.5	56		Put copper in.
9.50	2805.0	8.5	56	6550.99	All melted.
10.00	2812.5	..	..		Start to pour 1135° C.
10.15	2812.5	8.5	35		Put silver in.
11.00	2854.0	8.5	50	7462.20	All melted.
11.15	2875.5	8.5	50		Started to pour.
11.30	2875.5	8.5	35		Put silver in.
12.15	2915.0	8.5	50	7500.00	All melted.
12.25	2926.0	..	..		Started to pour.
12.40	2926.0	8.5	35		Put silver in.
1.35	2968.5	8.5	50	7500.00	All melted.
1.50	2979.0	..	..		Started to pour.
2.15	2979.0	8.5	35		Put silver in.
3.50	3034.0	8.5	45	7545.30	All melted.
4.00	3044.0	..	..		Start to pour.
Totals..	316.7			36558.49	

Rate of Melting

Melt	Melting Time Only Lb./KW.H.	Melting and Superheating Time Only Lb./KW.H.	Material
1	9.8	8.4	Fine silver and copper
2	12.3	8.15	Sterling scrap
3	12.7	10.2	Sterling scrap
4	12.1	9.7	Sterling scrap
5	9.4	8.0	Fine silver and copper
Average..	11.3	8.89	

Rate of melting: Average for all the time, 7.95 pounds per KWH.

avoided the use of a rather fragile quartz cylinder), which mate-
quency converter which energizes it from the photographs repro-
duced in Figures 12 and 13.

Figure 12 shows the furnace in its down position, and Figure 13 when tilted for pouring.

Figure 3 is a photograph of the three-phase high-frequency converter set which energizes the furnace. The set contains no transformer, as it is designed to operate directly from the three-phase, 60-cycle 6,600 volt service.

The performance of this furnace mechanically, electrically and metallurgically appears to be quite satisfactory. It is capable of continuous operation for eight hours or more and is actually being operated at the Handy & Harman plant throughout a working day.

Table I shows the performance of one day's operation, and may be taken as typical of what the furnace is capable of doing.

It may be said in conclusion that the highly useful accomplishments of high frequency inductive heating are simply unlimited—provided high frequency power is available in commercial quantities, and at a cost which is not prohibitive. Certain it is that high frequency converters, of a static character, are now available at reasonable price in single units up to 60 kilowatts, and that these units may be multiplied for operating a single large furnace without undue complication.

Tests have shown that with a suitably designed furnace for a load the efficiencies of these static converters—which operate on the principle of oscillatory currents—are quite the equal of the best performance of high frequency alternators which have been built.

Two years' experience in building and operating many high frequency equipments—over five hundred kilowatts were in service at the end of last February—have proved beyond a doubt that the principles of high-frequency induction presented before this Society in April, 1919, are perfectly sound, and both laboratory and commercial installations have been made which show that this new method of electric heating has come to take its place with other electrical methods of heating for the permanent service of science and the industries.

Trenton, N. J.
March 1, 1921.

DISCUSSION.

J. A. SEEDE[1]: I would like to ask Dr. Northrup if he can tell us how that aluminum carbide coating resists cracking as the crucible heats and cools? Also, how it resists abrading when the stuff is hot.

E. F. NORTHRUP: The lining is put on as follows. In describing the process to you you will see that it requires a furnace of the high frequency type to produce the necessary heat.

Alundum powder is first taken and mixed with water to a creamy consistency. The inside of the crucible is filled with this. It is then poured out in a manner to leave an even, thin coat of alundum over the inside surface of the crucible. The crucible is then set in a gas oven until thoroughly dried.

Another mixture is then made of fine carborundum powder and silica about two-thirds carborundum and one-third silica powder. To this is added a little alundum. This mixture is wet with water until it is a creamy consistency. The crucible is filled with this and the contents quickly poured out so as to leave a second thin coat over the first coat of alundum. The crucible is again dried in a gas oven. It is then placed in an inductor coil and surrounded with a heat insulator of lampblack. To prevent the lining, when raised to a temperature which will melt alundum, from running down the wall of the crucible and gathering in the bottom it is found necessary to fill the crucible with a mixture of carborundum fire-sand and ground up Acheson graphite in proportions of about half and half. The crucible is now heated by high frequency current to a temperature such that silica fumes begin to come off copiously. The crucible is then allowed to cool to a point where it can be lifted with tongs out of the lampblack.

The mixture of carborundum fire-sand and Acheson graphite does not sinter and will pour out of the crucible. If everything is done exactly right, what happens is that the alundum melts and is partially reduced where it is in contact with the graphite wall of the crucible and forms a hard coherent coating.

To coat a crucible in this manner requires some means of heat-

[1] Electrical Engineer, General Electric Co., Schenectady, N. Y.

ing the crucible quite uniformly to a temperature of about 2,100° C., and the author is not aware of any type of furnace which will do this in the manner required other than the high frequency induction furnaces.

To make a coherent and smooth lining on the inside of the crucible requires quite a little practice, but if the process is properly carried out, very excellent results may be obtained.

Such a crucible may be heated to a temperature of about 1,800° C., and its inside freely exposed to air without oxidation.

We have had very little trouble with the lining developing cracks, but it is quite difficult to get the lining satisfactorily smooth.

F. A. J. FitzGerald[2]: I have also had some experience with putting linings and coatings in crucibles to protect them in the way Dr. Northrup has described, and Mr. Seede's point is a good one. I think Dr. Northrup will find out eventually that even when he gets a good adhering coating it will crack owing to the difference in the coefficient of expansion by heat of the carbon and the coating. Minute cracks will form and the carbon will burn underneath. I have coated long carbon tubes with silicon carbide, and an examination of the cross section of the tube when broken showed a perfectly adhering coating. Even when the tubes had been used for some time they appeared perfectly free from cracks in the coating. Finally, however, the carbon tube burnt out, leaving the silicon carbide coating in the form of a series of rings. Circumferential cracks had occurred in the silicon carbide coating owing to the difference between its co-efficient of expansion by heat and that of the carbon tube.

Dr. Northrup did not mention what is one of the most important characteristics of any protective coating of this kind, *viz.*, the same coefficient of expansion by heat as that of the carbon or graphite.

J. A. Seede: Do you mean that the cracks opened up?

F. A. J. FitzGerald: Yes. Will Dr. Northrup tell us if he has graphitized any fairly large pieces of carbon in his furnace, and, if so, whether the extremely rapid heating does not tend to cause cracking?

[2] FitzGerald Labs., Inc., Niagara Falls, N. Y.

COLIN G. FINK[3]: In support of Dr. Northrup and in contradiction to Mr. FitzGerald, I wish to state that this lining proposition has been tackled before, with all due respects to Dr. Northrup's experiments. A very interesting correlated case is the fusing of low expansion glass to ordinary high expansion glass. Take a glass with a coefficient of about 0.0000036 and fuse this directly to a glass with a coefficient of about 0.0000085 and you will never get a permanent joint. But on the other hand, absolute vacuum-tight seals are being made every day by interposing two or three glasses having coefficients intermediate between 0.0000036 and 0.0000085. These seals will withstand a range of temperature of over 300° C. The same principle that applies to glasses applies to crucible linings. If you have a crucible with a coefficient of expansion of about 0.000005 (the coefficient of most crucible materials is comparatively low) and you wish to apply a lining that has a coefficient of expansion of about 0.000008, without any intermediate graded layers your lining is bound to crack or spall. The whole trick is in properly grading the lining layers.

E. F. NORTHRUP: That is exactly what I got.

F. A. J. FITZGERALD: I have found that even when coatings or linings worked very well with small crucibles they failed when dealing with large crucibles.

COLIN G. FINK: I really do not see that that would make any difference.

L. E. SAUNDERS[4]: I would suggest to Dr. Northrup that he try a lining of sintered magnesia in his crucible. If he uses finely powdered sintered magnesia, a layer a quarter of an inch thick, and heats it up to about 1,600° C., he will get a very impervious lining, one that will stand temperature as well as the other conditions very well indeed.

[3] Consulting Electrometallurgist, So. Yonkers, N. Y.
[4] Norton Company, Worcester, Mass.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 22, 1921, President Landis in the Chair.

THE REGULATION OF ELECTRIC STEEL ARC FURNACES USING MOVABLE ELECTRODES.[1]

By W. G. Mylius.[2]

Abstract.

A discussion of the difficulties of operating arc furnaces for melting steel, particularly when melting cold scrap, and of the kinds of arc current regulators which have been devised to maintain some function of the power input constant, such as current, voltage, watts, or a combination of these. Difficulties caused by the weights and inertia of the electrodes are considered, and the phenomena of "hunting" explained. A new form of electrode regulator is described and illustrated which will operate with greater precision and at higher speeds than previous types, and thus overcome the difficulties of "hunting." [J. W. R.]

It was about 1878 that Siemens conceived the idea of melting steel commercially by the use of the electric arc. Siemens' work was followed by that of Stassano, an Italian; Girod, a Swiss electrical engineer; Heroult, and others. Various types of furnaces have been designed in past years, but in the steel industry the tendency seems to be toward the adoption of the type invented by Heroult, in which all the current is brought to the furnace through vertical electrodes and where the arc forms between these electrodes and the bath.

The mechanical difficulties in operating the electric arc furnace have been overcome one by one until the mechanical design now leaves little to be desired. However, one difficulty which has retarded the development of the steel furnace is the maintenance

[1] Manuscript received March 7, 1921.

[2] Electric Furnace Engineer, Westinghouse Elec. & Mfg. Co., East Pittsburgh.

of some function of power input in the furnace constant. The most convenient method of controlling the power input is by raising and lowering the electrodes. The difficulty incurred, however, in attempting to move such large masses is apparent, and the inherent instability of the electric arc adds materially to the problem.

It has been a well-known fact for many years that the electric arc is inherently unstable. That is, for an arc of given length, the voltage across the arc will decrease as the current increases. On a constant potential circuit, therefore, it is necessary to use a resistance, or in alternating current systems a reactor, to protect the equipment.

In the early stages of the arc furnace development it was possible to utilize resistance or reactance as the sole stabilizing medium. However, it is evident that as the power drawn by the furnace increases, such a method becomes decidedly uneconomical. Even if it were economically practical to control the power drawn by the furnace with reactance or resistance, in a furnace melting down cold scrap, in which the arc forms between the electrodes and the material to be melted, there still remains the necessity for a device to maintain approximately a constant arc length as the material melts.

It was the practice of early installations to control manually the position of the electrodes to maintain as nearly as possible a constant length of arc. Obviously the regulation obtained by such means is crude at best. As furnaces have grown in size and number and as power companies have increased their restrictions and penalties on drawing large blocks of power even for short intervals, the need for a regulator that will automatically control the position of the electrodes in such a way as to maintain some functions of the power input constant has increased to such a point that the efficiency of melting metals in the arc furnace is very largely dependent on the efficiency of the regulating devices.

Electric arc furnace development has resulted essentially in two types of furnaces.

1. The type in which the electrodes enter the furnace vertically and are raised and lowered by means of a steel cable passing over

a motor-operated winch. Furnaces of this type have found almost universal adoption in the steel industry.

2. The type in which the electrodes enter in a horizontal or nearly horizontal direction and are operated by a motor-driven worm. The Rennerfelt furnace is of this type and is used for brass melting and, to a lesser degree, for steel.

It is the problem of the regulator engineer so to control the position of the electrodes automatically with respect to the furnace charge that one function of the power input will remain substantially constant, regardless of other conditions within the furnace.

The early experiments with the electric-arc light demonstrated conclusively the difficulties incident to applying an automatic regulating device to an electric arc. The problems to be overcome there, however, were not as great as those connected with the arc furnace, for the reason that the mass of the moving parts in the arc lamp are small enough to permit of direct control, whereas the mass of the electrodes of the arc furnace is so large that several relay stages are required to permit small fluctuations in power to operate the massive electrode-operating mechanism. On account of the mechanical and electrical inertia of the system, a time-lag exists between the change of the regulated quantity and its effect on the position of the electrodes. With so many steps in the regulating system and with such large masses to control, it is essential that the regulating device be quick to respond and that the restoring speed shall bear some relation to the magnitude of the power surge.

To those familiar with the art of controlling an unstable quantity, it is well known that in attempting to obtain high speed and precision, a condition known as hunting is invariably encountered. By hunting, is meant the continuous periodic surge of the quantity being regulated.

When an elementary control is employed to maintain an unstable quantity constant, it is necessary to either operate at low speeds or to be satisfied with reduced accuracy or to strike a compromise on both.

Among the functions of the power input into the furnace, which can be utilized to actuate a regulator may be mentioned current,

voltage, watts, or a combination of these. Most steel and brass furnaces utilize either current or voltage or the two combined, whereas a watt-controlled regulator has been applied to abrasive furnaces and to the control of pulp mills.

An elementary form of regulator, consists of a control element which is usually a contact-making ammeter or voltmeter, connected to the circuit, supplying power to the furnace. It is provided with two pairs of contacts one pair closing when the quantity being regulated is above normal, and the other closing when the quantity is below normal. When the current is normal both contacts are open. Each pair of contacts operates its own contactor, which in turn controls the electrode motor, either in a lowering or a raising direction.

Such an elementary device is limited in its application, as will be appreciated when an examination is made of its operation. Assume that the furnace is drawing normal current; both contacts on the control element will be open and the motors will be at rest. A sufficient change in the furnace conditions will close one of the contacts, which will operate the corresponding motor in a direction to compensate for the change. As the motor adjusts the electrode, the regulated quantity will approach normal, and when it reaches the value for which the regulator is set, the control element will disconnect the motor from the line and apply dynamic braking. Owing to the instability of the arc and the inertia of the moving parts, however, the motor will drift somewhat, and if a fairly high electrode speed is used the electrode will overtravel a sufficient amount to change the regulated quantity to the opposite side of its normal value. The motor will then be reversed and the electrode will move in the opposite direction.

The result may be a perpetual moving condition, after once being started, which, as stated before, is known as hunting, or, if the amplitude of each surge is less than the preceding one, the system will eventually come to rest. In an elementary device, hunting is overcome by making the position of the control element lever dependent on the quantity being regulated and by separating the contacts far enough, so that after one contact has been opened, the change in the regulated quantity, due to mechanical drifting

of the electrode mechanism, and to the electrical inertia, is not sufficient to close the other contact, which would operate the motor in the reverse direction. To obtain such a condition, low electrode speed and a comparatively wide zone is necessary.

A type of regulator which obviates the hunting difficulty to a large extent has been in use for a number of years and is giving satisfaction. Instead of operating the electrode motors continuously, it applies current to them in a series of impulses, that is

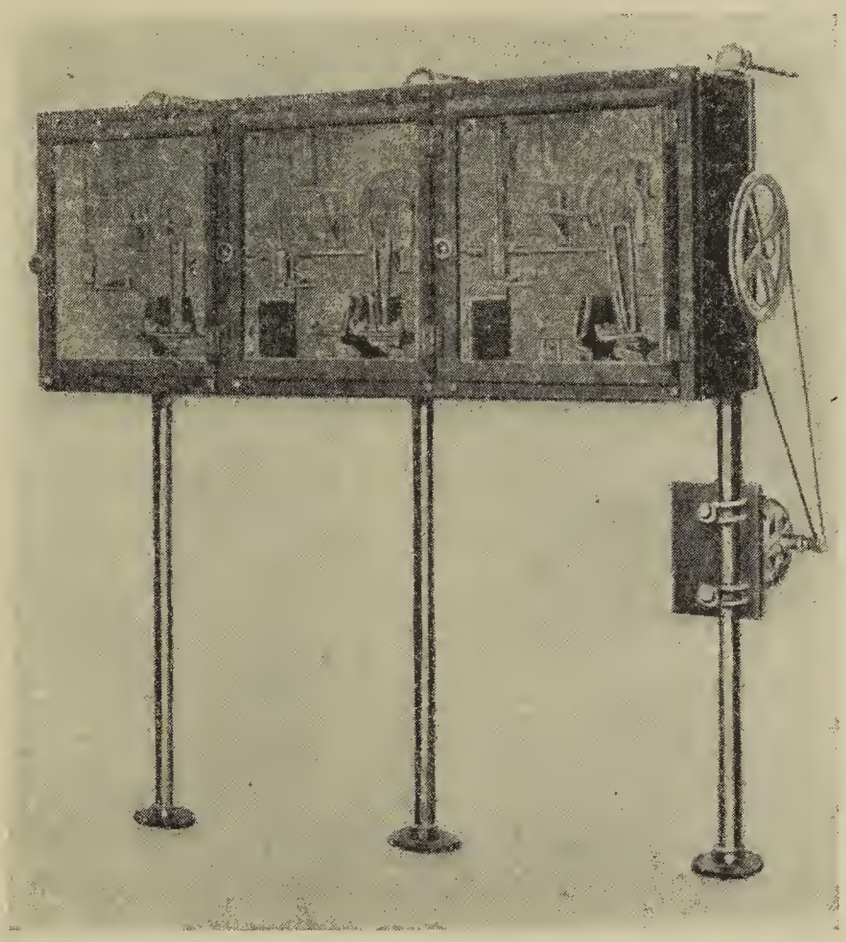


Fig. 1. Step-by-Step Regulator.

when the quantity being regulated deviates from its normal value the electrodes are moved in a series of steps. If the change in the regulated quantity per step is smaller than the value necessary to cause the controlling device to reverse the motor, the regulator will not hunt. Such a regulator is known as the step-by-step type, due to its method of operation.

Fig. 1 illustrates a Thury regulator which is a typical regulator of this type. It is actuated by current alone, and is thus limited in its application as will be shown later. This type is familiar

to all furnace men and a detailed description is therefore unnecessary.

The elementary type and the step-by-step type of regulators have been in use for a number of years and are now controlling

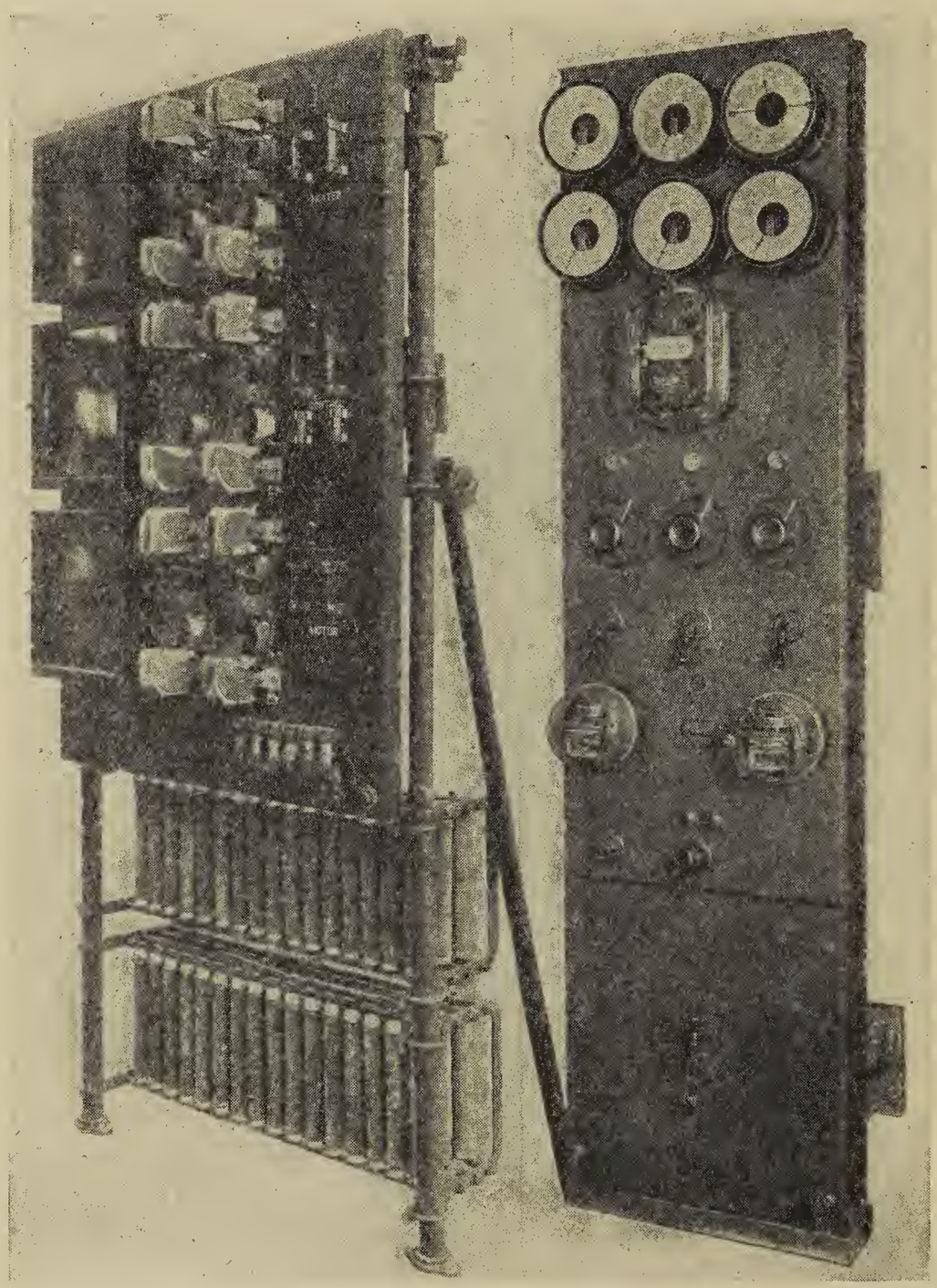


Fig. 2. Switchboard with Control Equipment (Front View).

Fig. 3. Regulator Panel (Front View).

the majority of the electric arc furnaces throughout the country. However, steel men have appreciated for some time that a more accurate and rapid regulator would be desirable.

In an attempt to satisfy this demand, development was started

several years ago on a regulator which would, as far as possible, eliminate the shortcomings of those previously developed, and which would, therefore, supply some of the desirable features which the earlier types lacked. The outcome of the development is a regulator which will operate with greater precision and at higher speeds than the previously mentioned type.

The final form in which the regulator is being placed on the market is shown in Figs. 2 and 3, and the operation may most easily be understood by referring to the schematic wiring diagrams, Figs. 4 and 5.

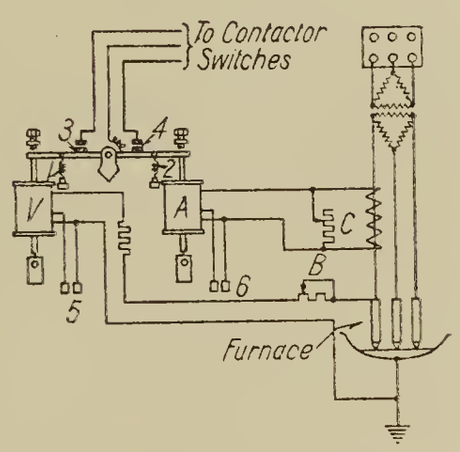


FIG. 4. Schematic Diagram of Control Element Circuit.

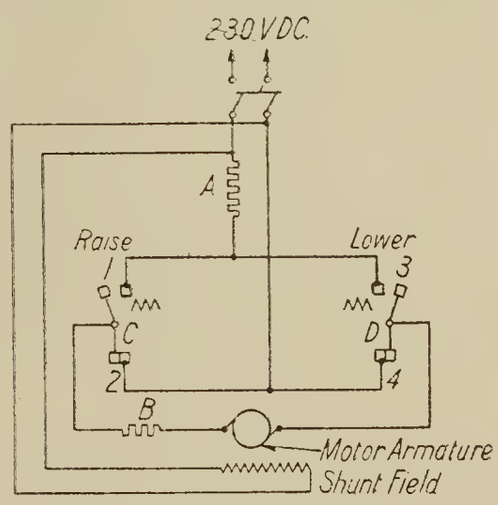


FIG. 5. Schematic Diagram of Electrode Motor Circuit.

The two sets of contacts *3* and *4*, Fig. 4, control the electrode operating motors through the medium of magnetically operated contactors, which are mounted on the regular panel. Assuming that the furnace is about to be started, an inspection of Fig. 4 will show that neither of the solenoids on the main control element *V* or *A* will be energized while the main circuit-breaker on the high voltage side of the transformer is open. Under these conditions the two springs *1* and *2* will hold the lever in a horizontal position, maintaining contacts *3* and *4* open. On closing the main breaker a potential will be immediately created between each electrode and the shell of the furnace. Voltage coil *V* is now energized and pulls up on its core, closing contact *3* and operating the electrode motor in a direction to lower the electrode continuously and at full speed until it makes contact with the bath. As the voltage coil is connected between the electrode and the furnace shell, its current will be shunted and it will become

de-energized the instant the electrode makes contact with the steel, thus allowing the lever of the main control element to return to its horizontal position and open the motor circuit. As no alternating current can exist in any electrode until two or more are in contact with the bath, current coil *A* will not be energized until one of the other electrodes is lowered a sufficient distance to strike the bath. As soon as the circuit is completed, current coil *A* becomes energized. Contact *4* is thereby closed, which causes the electrode motor to raise the electrode, thus drawing an arc to the bath. The sequence of operations is similar for the remaining electrodes. The motor continues to raise the electrode until the voltage between it and the bath increases and its current decreases to such an extent that the pull of coil *A* is equivalent to that of coil *V*. The lever will then assume a horizontal position, opening the motor circuit. Any disturbance of the equilibrium between the pull of coils *A* and *V* due to the variations in the arc will cause either contact *3* or *4* to close, thus operating the electrode in a direction to compensate for the disturbance.

Current adjusting rheostat *C* is connected across the current transformer, and by changing its position the value of the current per phase for a given current in the current coil of the element can be altered at will within the limits of the apparatus. This current can be varied approximately 20 percent of the normal value.

Auxiliary contacts *5* and *6* are mechanically attached to, but insulated from, the magnetically-operated contactors which control the electrode motors. Contact *5* closes when the "lower" contactor closes, and contact *6* closes when the "raise" contactor operates. These contacts therefore shunt respectively a part of coils *A* and *V*, and after the lever has been moved in a direction to operate the "raise" contactor, the corresponding auxiliary contact will close, thus shunting a part of coil *A* and tending to restore the lever to its horizontal position. If the change in pull is sufficient to allow the lever to operate, its contacts will separate and allow the contactor to open. If during the time that the contactor was closed the motor has not moved the electrode a sufficient distance to adjust the current to the value for which the regulator is set, the pull of coil *A* will still overbalance that of

coil *B*, and the "raise" contactor will again close contact *4*. A vibrating condition will thus be set up between the control element and the contactor. If the current per phase is more than approximately 15 percent. on either side of its normal value, the change in pull on short-circuiting a part of the winding on coil *A* by the auxiliary contacts will be insufficient to allow the core to drop. The contactor will therefore remain closed and the electrode motor will operate continuously in a direction to compensate for the abnormal current. As soon as the current reaches to within approximately 15 percent of its normal value the change in the pull on the solenoid *A* when the auxiliary contact *5* closes is sufficient to allow the core to drop out and to bring the lever to its horizontal position. Between this 15 percent point and the normal value of the current the regulator assumes a vibrating condition, and the motors are subjected to a series of impulses, the average time the motor is connected to the circuit being a function of the amount the furnace current deviates at any particular instant from its normal value.

There are two distinct stages, therefore, in the operation of the regulator, one being the continuously-running stage and the other the vibrating stage. The vibrating feature permits the motors to operate at a high speed until the current in the electrode has been brought back to within 15 percent of normal (approximately), when the speed is gradually reduced to zero. High speed and freedom from over shooting are thus obtained.

This feature is of great importance, since with previous types of regulators, especially with the elementary contact-making ammeter type, there exists a zone of considerable extent within which the regulator will not respond. This great lack of sensitiveness in a regulator, together with the congested ammeter scale on low power, makes it so difficult to accurately balance the currents in the several electrodes that it is quite possible for an electrode to get down into the bath and give off carbon to the metal without the knowledge of the melter, when the furnace is being run on low power awaiting the result of a test.

With the voltage element, as embodied in the new regulator, it is impossible for an electrode to run down into the bath, even if the current in the other electrodes fail. For example, if the

electrodes are all withdrawn by hand control and one electrode is put on automatic control, it will descend only until the electrode makes contact with the bath. It is impossible for the electrode to come in contact with the steel. This feature will be particularly appreciated when the furnace is producing low-carbon steel.

The voltage element in the control of each electrode makes each regulator independent of the others. For instance, in a three-phase furnace, operating with balanced currents in the electrodes, one electrode may be withdrawn without disturbing the equilibrium of the other two. With simple current regulators any change of current in one electrode disturbs both the other regulators.

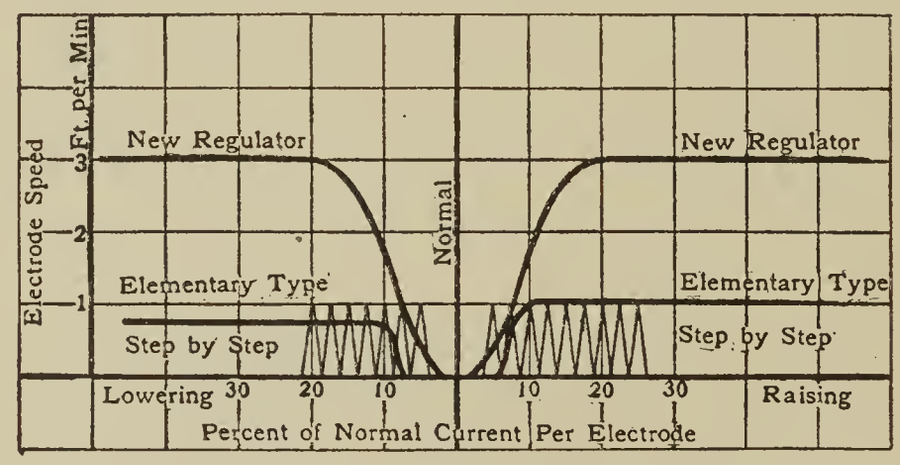


FIG. 6. Characteristic Curves of Different Types of Regulators.

The voltage element also serves as a no-volt release. The control element is mechanically balanced with all power off, so that both main contacts are open; hence, if the power fails, the control levers instantly come to equilibrium between the main contacts, all contactors drop out, and the electrode motors stop. No other no-voltage release feature is necessary.

Another feature of the regulator is the high electrode speed which it is possible to use. This is accomplished by making the motor speed proportional within certain limits to the amount the electrode current deviates from its normal value. It was explained above, how a vibrating condition of the contactors existed between the 15 percent deviation point and normal current, and how the part of the time that the motor is connected to the line is a function of the amount the current deviates from its normal value. The average speed of the electrode motor varies

therefore from practically full speed to rest, along some curve similar to that shown in Fig. 6.

The value of high speed will be readily appreciated. It permits the furnace to be put on automatic regulation on a cold charge, thereby making hand-regulation unnecessary. The regulator will also rapidly correct for small changes in arc condition. When melting down a charge of light material, the tendency is for the electrode to bore through the charge, which later falls in around

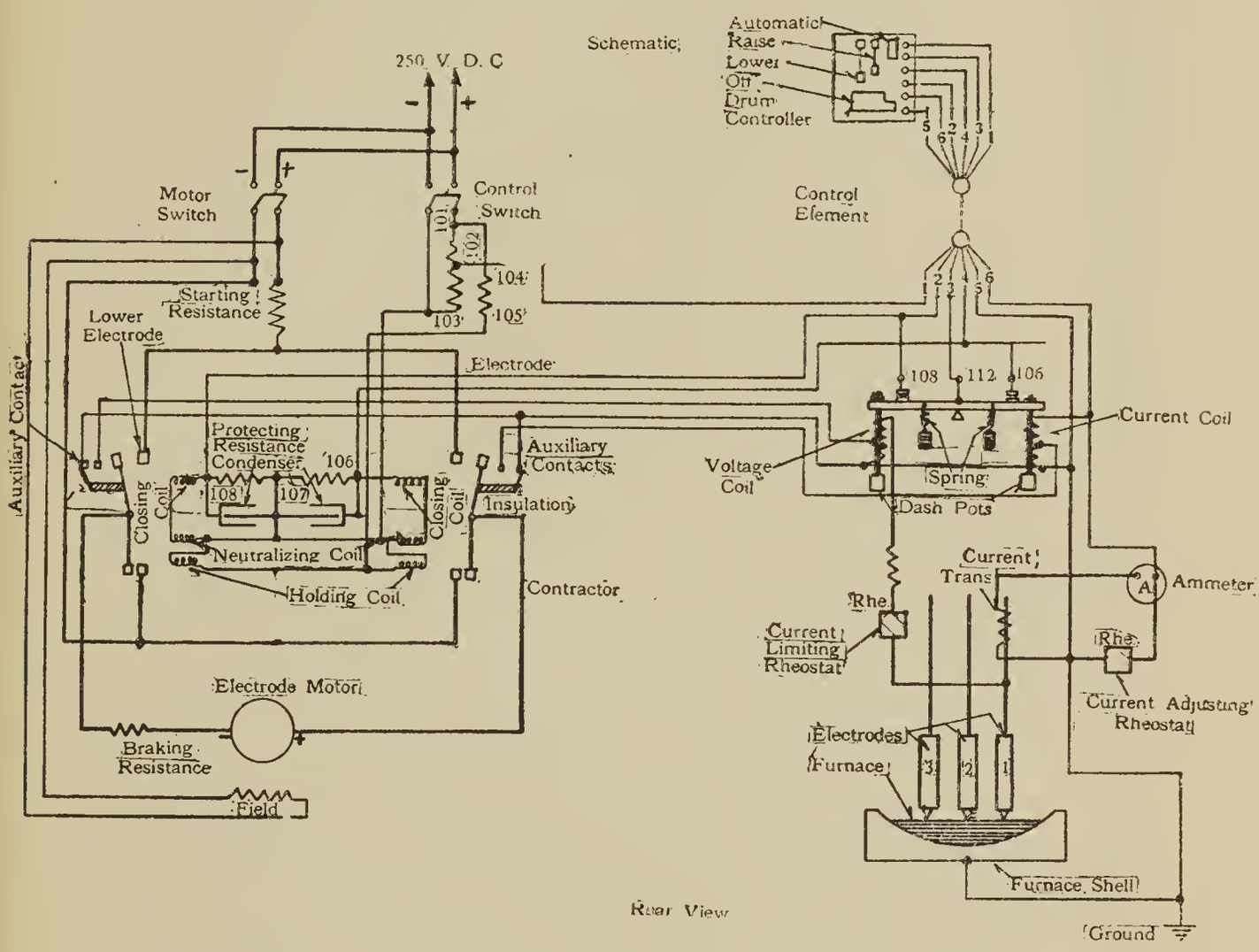


FIG. 7. Complete Schematic Diagram. For One Electrode.

it, causing an abnormal rush of current and tripping the breaker, unless the regulator is extremely rapid. The new regulator will extricate the electrode in a large majority of cases before the breaker is tripped.

A schematic diagram of one electrode motor circuit is shown in Fig. 5. *C* and *D* are two double-acting contactors, which start, reverse and apply dynamic braking to the electrode motor. *A* is a resistance in the supply circuit which acts as a starting resistance,

and *B* is a smaller resistance which acts as a braking resistance when the motor is brought to a stop. The shunt field is permanently connected to the direct-current supply circuit.

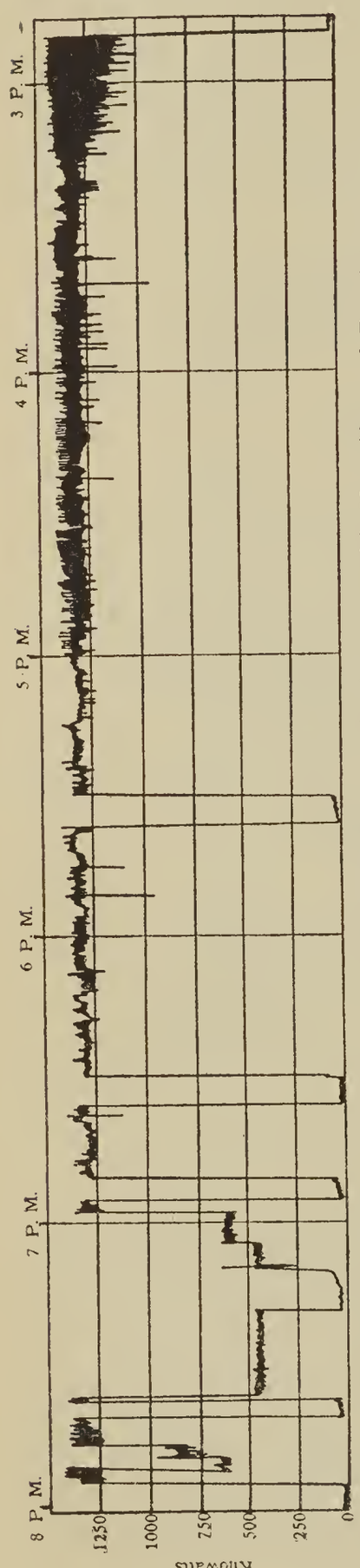


Fig. 8. Power Consumption Curve of Six-Ton Heroult Furnace—with New Type of Regulator.

If the current in one electrode has fallen below its normal value, the main control element will close switch *D*, thus connecting the motor to the line through resistances *A* and *B*. When the furnace current has reached its normal value, the control element lever will assume a horizontal position and contactor *D* will open contact *3* and close *4*. Contact *2* has been closed during this operation and the motor armature is now short-circuited through resistance *B*, thus applying dynamic braking to the armature. It is to these contactors that the auxiliary contacts are mechanically attached. Resistances *A* and *B*, Fig. 5, are adjustable by taps and therefore are adaptable to varied conditions.

It is obvious from the mechanical construction that the upper and lower contacts of any one conductor cannot be closed simultaneously. It will be further noted that even if both upper contacts should be closed at the same time, the armature will be shunted through a resistance, and there is no possibility of short-circuiting the line. This is accomplished without the use of interlocks.

Fig. *7* shows a complete schematic diagram for the control and operation of one electrode.

Fig. 3 shows the regulator panel upon which are mounted the contactors and control elements as well as fuses, knife-switches, etc., etc.

All of the control equipment which the melting crew are required to handle is mounted on a separate panel, shown in Fig. 2. The regulator panel can, therefore, be set up in some more protected place than the furnace room, if desired.

A typical curve taken with a direct-acting graphic watt-meter on a six-ton Heroult furnace melting cold scrap and making alloy steels is shown in Fig. 8. The regulator was put on automatic control at the start on a cold charge and the short time in which the furnace settled down is interesting, the absence of high current peaks is also noteworthy. A high-speed regulator would be expected to keep down demand peaks, and the curve seems to justify this expectation. However, the degree of regulation is effected to a great extent by the method used in charging the furnace, and if no attention is given to the manner in which the charge is built up, it may require an appreciable amount of time before steady conditions are obtained. Instantaneous surges, of course, will be encountered until a pool of molten metal has been formed at the bottom of the furnace, but with a rapid regulator they will not be of sufficient duration to appreciably affect the demand rate.

The electric arc furnace in metallurgy has unquestionably come to stay, and the number of installations will undoubtedly increase from year to year. However, the efficiency obtained in this method of melting and refining metals will in no small measure be governed by the effectiveness of the regulating device, and the perfection attained in the finished product will depend very largely on how faithfully the regulator performs its duty. The metallurgist must look to the regulator engineer, therefore, for assistance and co-operation, if he is to continue the commendable strides that he has made in past years toward the goal of better and cheaper metals.

DISCUSSION.

Colin G. Fink[1]: How does your regulator differ from others?

W. G. Mylius: The main features of our regulator are freedom from hunting, high electrode speed, on both hand and auto-

[1] Consulting Electrometallurgist, So. Yonkers, N. Y.

matic regulation, and a very narrow zone of regulation, if desired. The electrodes are independent of one another, *i. e.*, one electrode may be operated by hand or cut out entirely without affecting the regulation of the other two. The voltage coil absolutely prevents the electrodes from running down into the bath and permits of starting the furnace with automatic regulation on a cold charge, and continuing so throughout the heat.

M. H. BENNETT[2]: Does it raise the power factor of the furnace by substituting your regulator for an ordinary ampere regulator?

W. G. MYLIUS: No, the power factor of any given furnace, installation is a function of the current drawn by the furnace, and of a given power input into the furnace. The regulator will not directly affect the power factor. However, by making the power input into the furnace more uniform, the regulator does tend to improve the average over all power factor.

JAMES KELLEHER[3]: On page 360 Mr. Mylius speaks about the drifting of the electrodes, and amongst others he mentions the fact that the increase of the current after the regulator has ceased to operate is due to the induction of the furnace circuit. Could not this be due to the effect of second-class materials? Could not the increase of current in the furnace be due to the decrease in resistance?

W. G. MYLIUS: Yes, it could be.

JAMES KELLEHER: Not so much to the induction of the circuit. Another thing I would like to ask, what is the sensitiveness of the regulator? That is, before it commences to actuate? What increase and decrease of current is necessary before the regulator operates?

W. G. MYLIUS: It is generally set to operate within a zone of 10 percent.

JAMES KELLEHER: You have shown on the characteristic regulating curves of furnaces for this step by step regulator a speed value of approximately three percent, plus or minus; is that correct?

[2] Research Engineer, Scovill Mfg. Co., Waterbury, Conn.
[3] Assistant Engineer, Goderick, Ont., Canada.

W. G. MYLIUS: I did not take that curve, but I would say that it was approximately correct.

JAMES KELLEHER: The step by step regulator according to the curve then, is not as sensitive a regulator as the one which you mentioned and described in your paper, and yet your regulator only operates plus or minus ten percent, whereas the regulator which is the step by step regulator will operate plus or minus three and a half percent for normal steel furnace operation, and for closer operation such as carbide furnace, will operate one and a half percent plus or minus.

W. G. MYLIUS: There is a ten percent zone, that is, five percent either way from normal, which we have found from experience to be close enough for the average steel furnace, and we believe this to be a much smaller zone than that used by the majority of furnaces in operation today. However, you will see on the characteristic curve chart that it is possible to set this regulator to very much closer limits if desired.

JAMES KELLEHER: Have you ever studied the arc form in the case of hunting?

W. G. MYLIUS: I have not.

JAMES KELLEHER: I think you will find, on studying the alternating current arc, that one of the causes of hunting is due to the action of the electric arc in the electric arc furnace. I think I described that last fall in a paper on Electric Arc Phenomena in Furnaces (These Trans., **38**, 309).

E. L. CROSBY[4]: I understand Mr. Kelleher to say that the regulator he mentions will regulate to within three and one-half percent without hunting.

JAMES KELLEHER: If the regulator adjustment maintains flow after it commences to operate and increases the current one and a half percent of the load, of course the furnace will increase above that one and a half percent, but will always be brought back, except under abnormal conditions.

E. L. CROSBY: It has always seemed to me that from the standpoint of the electric circuit, the regulation of the electric arc

[4] Vice-President and General Manager, Detroit Electric Furnace Co., Detroit, Mich.

furnace is always under abnormal conditions. It is of no importance when the regulator may start to operate, provided it does check the surge rapidly and bring the load back to approximately normal rather rapidly. I was quite astonished to hear that the regulation was within three percent, because my experience with several furnaces on the power system in which I was formerly interested did not lead to any such figures; 15 percent and 20 per cent would be better.

James Kelleher: The normal operation of an alloy furnace will allow that condition, the regulation from one to two percent above or below normal, and in the furnace load, within approximately five percent plus or minus. That is at the peak. In the case of abnormal conditions of the furnace, you are liable to get surging in the furnace if the bulk of metal has been allowed to become too hot. In steel furnace operation, once the charge is melted down and you have a slag, you will get the normal product that is passed from furnaces. Then when you put in some such addition as ferro-manganese, you will have abnormal conditions which, so far as I know, are more or less instantaneous, and no mechanical device could take care of these excessive surges.

E. L. Crosby: The difficulty seems to me to be that we discuss the steel furnace operation from the wrong viewpoint when we are discussing regulation; except for the fact that we would like to get the current into the steel as fast as possible, it makes no difference to the operator of the furnace whether the load is continuous or not. The real reason he is interested in the regulation is because the power company is going to charge him excessively if he does not have it, and that being the case, it is necessary to talk about regulation. After you melt down, you can control any fairly well-operated furnace with hand regulators, after you have your bath formed, without any material difficulties, but during the melting down process, it is quite a man-sized job to keep the input anywhere near normal.

J. A. Seede[5]: Up to 1912 or 1913 the step by step regulator had the field to itself. When using that regulator the maximum electrode speed, with the motor running continuously, was about

[5] Electrical Engineer, General Electric Co., Schenectady, N. Y.

three feet per minute, but as the step by step feature opened and closed the motor circuit from 60 to 100 times per minute, the average electrode speed, that is, the effective speed that draws the electrode away from the danger zone or brings it back to the point where the arc is struck, was six to seven inches per minute. About that time, believing that the step by step regulator was not wholly successful, developments were commenced which resulted in bringing out the continuous movement regulator, in which the electrode is moved steadily from one position to another at a speed varying between 8 and 15 inches per minute, that is, at a considerably higher effective speed than the step by step regulator. I wish to point out that a mere statement of electrode speeds corresponding to the free running speed of the motor means nothing as far as successful regulation of the furnace is concerned; the average effective speed is the speed that must be considered.

Now, as I understand from reading this paper, this new regulator is a combination of the intermittent and continuous movement types, and, as such, the maximum electrode speed does not indicate the results that will be obtained; as Dr. Northrup pointed out a short time ago, at least 75 percent of the success of any device depends upon its value after long periods of operation, and I think we must gauge the value of this regulator by the service it delivers in commercial operation. There are a number of points in the paper that would be of greater value if they were explained in detail, but our time is rather short. Mr. Kelleher brought up a point that was also not clear to me, that is, the statement is made that the induction of the circuit may cause the current to rise somewhat and cause hunting. In the ordinary 25-cycle circuit the induction changes and passes through zero 50 times per second, and in a 60-cycle circuit, 120 times per second. Accordingly, it is not clear to me how the induction of an alternating circuit can change appreciably after the electrode has come to rest.

M. H. Bennett: I have given this question of electrode furnace control a considerable amount of study over a period of about eight years, and I cannot understand this statement that that control is only sensitive within five percent or even ten percent or two percent. I do not see why a volt-watt or volt-ampere control differentially connected cannot be adjusted to work at least within

one-half of one percent, or a tenth of one percent. The trouble is that the furnace controls have all had a lot of dampening on the elements so that they did not move quickly enough because the reversing switches were poor. Where you want to look for your trouble is in your reversing switch. What we want to do in electric furnace control is at all times to maintain maximum sensibility and at no time to sacrifice the sensibility, but to put in there a time interval which will prevent over-shooting and hunting. I have seen electric furnace controls, not running at speeds other than Mr. Seede spoke of, under very severe conditions where currents were kept within one percent all the time without any trouble, and without any hunting, and with no brake on the motors; free running motors. I have seen speeds of 24 inches per minute (electrode speeds) with no intermittent operation at all, where two percent was maintained without any trouble.

W. G. Mylius: I would just like to say that, although a very narrow zone is possible with our regulator, we do not recommend it, as the wear and tear on the motor and mechanical mechanism of the furnace is too great.

W. S. Landis[6]: When I think of some of our carbide furnace electrodes having to be accelerated at some rather high speeds, the mechanical end of the problem seems to me somewhat more serious than the electrical side. Some of our electrodes with their holders weigh ten tons.

J. A. Seede: Of course we are not talking about the same kind of a fish.

W. S. Landis: We are using regulators throughout.

J. A. Seede: Yes, I appreciate that, and the continuous movement regulator is being used on that 10-ton electrode; we are talking about maintaining current constant with the continuous movement regulator. On those 10-ton electrodes the current is being maintained constant within three-quarters of one per cent. through the successful control of the continuous movement regulator.

[6] Chief Technologist, American Cyanamid Co., New York City.

W. K. Booth[7] (*Communicated*): I have read with considerable interest Mr. Mylius' paper and would like to ask several questions regarding operation which are not quite clear.

Referring to Fig. 4 on page 363, showing the schematic diagram of control element circuit and accompanying description, I do not understand where the potential is obtained for operating the contact-making voltmeter, lettered "V". At least it is not clear from the diagram.

With the delta connected transformers, is it necessary to use a "Y-connected" compensator to establish a neutral or is there an electrostatic potential, which can be depended upon to operate the coil? Or is there enough leakage so that the potential is established?

One further point: with a cold furnace and melting cold scrap, how is the voltage coil shunted when the electrode touches the steel scrap, as under this condition the resistance between the scrap, and the steel shell will be very high unless some special means are used to make connection?

When the furnace is hot with a basic bottom there probably would not be so much resistance, but with an acid hearth the resistance in passage of current will be much greater and we would expect, unless some special arrangement was made, that with acid operation the resistance would be so high that the electrode would be fed down continuously and would not stop when it touched the scrap or cold charge.

We would appreciate very much some expression as to how this difficulty is overcome.

W. G. Mylius: (*Communicated*): Where there is current flowing there is voltage also, and, although small, there is enough voltage drop between the electrode and ground to energize the voltage coil and cause the regulator to function as described.

If the charge is of high resistance or not properly built up in the furnace it may be necessary to make a metallic connection between the charge and the shell of the furnace until a pool of molten metal is formed; this is usually done by inserting a bar of metal into the charge and letting the end rest against the frame of the charging door. This bar is withdrawn after the furnace is

[7] Secretary, Booth Electric Furnace Co., Chicago, Ill.

heated up enough to be conductive. The method described above is also used for burning in the linings of a newly lined furnace.

With acid lined furnaces it is necessary to use metal rods or inserts of some form which are connected to the shell and extend up through the lining, as this form of lining is a poor conductor even when hot. It will be necessary to use care in charging so that some of the material is in contact with these inserts, otherwise it will be necessary to use a bar as described above until a pool of metal is formed in the bottom, which will insure contact with the inserts and the shell.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

REDUCTION BY MEANS OF SILICON.[1]

By Louis Kahlenberg[2] and William J. Trautmann.[3]

Abstract.

After a review of the work done in this field, the authors describe their own experiments. Silicon powder containing 95 percent Si and 5 percent Fe was used, ground to a fine powder. The substance to be reduced was mixed with the silicon and either (1) heated in a glass tube over a gas burner, or (2) put into a crucible and ignited by a primer of potassium chlorate and magnesium, or (3) ignited in a crucible by two silicon points between which an electric arc was produced. The latter was the unique part of the investigation, since it caused reaction in many cases in which the other methods failed. The results of numerous experiments are given—too numerous for abstracting.—[J. W. R.]

I. INTRODUCTION AND CONSIDERATION OF PREVIOUS WORK.

While silicates are very abundant in nature and have consequently received a great deal of attention on the part of mineralogists and chemists, silicides, which are artificial products whose formation involves the use of high temperatures, have been prepared and studied almost exclusively in recent years.

Many of the silicides may be prepared by the use of metallic silicon, but the latter was not available in sufficiently large quantities until the method of reducing silicon dioxide by means of carbon in the electric furnace was perfected. Indeed, since silicon became available in large quantities, the study of the reactions of this element with other substances naturally received special impetus.

[1] From a thesis submitted for the degree of Ph.D. at the University of Wisconsin. Manuscript received Feb. 25, 1921.

[2] Professor of Chemistry, University of Wisconsin.

[3] Graduate student, University of Wisconsin.

It is well known that silicon decomposes water at bright red heat, yielding hydrogen and silica. At white heat, silicon reacts with carbon dioxide forming silicon carboxide.

The following monographs were found especially useful as sources of information concerning the silicides:

1. "An Investigation of the Borides and Silicides," by Professor O. P. Watts, of the University of Wisconsin. This investigation, which was published in 1905, sets forth in a series of tables the most important physical and chemical properties of the silicides, and gives references to the original sources.

2. "Karbide und Silizide"—a monograph by Professor Otto Hönigschmid, of the Technical High School in Prague, published in 1914. Hönigschmid gives a historical summary, with references to the original sources, of what has been done in the investigation of the silicides. The discussion of the physical and chemical properties of each of the silicides is also given quite fully.

For information concerning the work done in more recent years, the current literature was consulted with the aid of the Chemical Abstracts.

Weiss and Englehard[4] describe the action of silicon on free nitrogen. They found that a series of nitrides of silicon is formed.

With some metals silicon combines directly to form silicides, in other cases it dissolves in the molten metal and crystallizes out when the melt cools.[5] Some of the important metals with which silicon forms silicides are calcium, barium, strontium, magnesium, cerium, glucinum,[6] manganese, copper, iron, nickel, cobalt, platinum, chromium, molybdenum, tungsten, titanium, thorium, zirconium, tantalum, uranium, vanadium, palladium, ruthenium, lithium. With the exception of the silicides of strontium, uranium, and tantalum, the silicides of the metals just listed have actually been formed by direct action of the element silicon upon the metal, or some simple compound of it. Among

[4] Zeit. anorg. Chem. (1910), **65**, 38.

[5] O P. Watts, "An Investigation of the Borides and Silicides." Bull. Univ. Wis., No. 145, Eng. Series (1906), **3**, 251-318.

Hönigschmid, "Karbide u Silizide." Monograph. der angew. Electrochemie, XLV; Knapp, Halle, 1914.

[6] Moissan, "Traite de Chimie Minerale," **2**, 402.

the important metals in which silicon dissolves and from which it crystallizes out on cooling are aluminum, silver, antimony, bismuth, tin, zinc, lead and gold.[7]

Lithium appears to be the only alkali metal which forms a silicide.

Silicon is known to be closely related to carbon in its chemical properties. Like carbon it has great affinity for oxygen, and so may act as a powerful reducing agent. The reducing action of silicon has been studied by a number of investigators.

Neuman[8] discusses the use of silicon as a reducing agent for oxides of metals of high melting point, notably tungsten, molybdenum and titanium. He concludes that all of the products contain silicon, the amount depending upon the metal whose oxide was reduced. He states further that the reduction of oxides of high melting metals by means of silicon is not practicable commercially, and that consequently carbon and aluminum really are the only reducing agents available for practical purposes.

Askenasy and Pounay[9] found that silicon reduces barium dioxide, forming the silicide of barium. They state that the reaction takes place with violence, and they mention the use of a mixture of sodium peroxide and barium peroxide with silicon in the reduction of other metallic oxides, such as chromic oxide. They also suggest that mixtures of silicon, barium peroxide and sodium peroxide may be used to obtain high temperatures, as in the case of the aluminum thermite reaction of Goldschmidt.

In the course of his investigations, H. Goldschmidt[10] describes some experiments on new thermite reactions in which he used silicon alone, and also silicon mixed with metallic calcium, and again with metallic magnesium as the reducing agent. He found that silicon alone does not reduce either Cr_2O_3 or Mn_3O_4 in such a way as to yield the metal in fairly pure form. When MnO_2 is reduced by silicon, the final product is also contaminated with that element. Silicon reacts slowly with Fe_2O_3 and not at all with Fe_3O_4. Again, while silicon reduces CuO and PbO, neither

[7] Watts, *l. c.*
[8] Zeit. Elektrochem (1908), **14**, 169-72.
[9] *Ibid.* (1908), **14**, 810-11.
[10] *Ibid.* (1908), **14**, 558-64. Reactions (1908), **3**, 48-52.

copper nor lead is obtained in good, pure form. In his report to the German Bunsen Society, Goldschmidt[11] further states that silicon reduces lime, forming a silicide of calcium.

Quite early Winkler[12] mentioned the fact that silicon reduces lead oxide, and that lead silicate is formed during the reaction.

H. N. Warren[13] states that a large number of metallic oxides when mixed with metallic or graphitoidal silicon are reduced, the silicon, of course, being oxidized during the process. Thus, litharge is reduced to metallic lead by silicon at a dull red heat with practically the same readiness as if carbon had been used. When an excess of silicon is employed, a brittle regulus is obtained which consists essentially of lead silicide. Copper oxide and other readily reducible oxides, when reduced with silicon, yield the pure metal or a corresponding silicide. Warren further states that "even metallic chromium is easily reduced by heating silicon together with the oxide of that metal, tungstic and molybdic oxides suffering a like decomposition."

A serious disadvantage of silicon as a reducing agent is the fact that the silicon dioxide, being non-volatile, does not leave the field of action as do the oxides of carbon. The silica which thus remains in the reacting mass tends to form silicates, which are not infrequently of the nature of a slag, throughout which the reduced metal or its silicide may be dispersed in the form of tiny globules, making it extremely difficult, and in some cases even impossible, to separate such particles from the slag. As has already been intimated, silicon also manifests a strong tendency to form silicides with a considerable number of the metals. This property is analogous to that of carbon forming metallic carbides. The silicides are usually very hard, brittle, crystalline compounds, whose properties are in a high degree determined by the nature of the metal which they contain.[14] The melting points of silicides are high, especially if they contain a relatively high proportion of silicon. Nearly all of the silicides react with the halogens at temperatures far below red heat. When heated in oxygen they are either oxidized superficially, or remain unaffected even at a high red heat. With few exceptions water

[11] Electrochem. Met. Ind. (1908), 6, 360-2 Iron Age (1908), 82, 232.
[12] Jour. prakt. Chem. (1864), 91, 195.
[13] Chem. News (1891), 64, 75.
[14] Hönigschmid, *l. c.*, 144

does not affect them, while the action of acid upon silicides depends greatly upon the individual nature of the particular compound in question.

According to Moissan[15], silicon will also reduce the oxides of certain non-metallic elements.

Attempts to use silicon as a catalyst have been few and they have not yielded positive results. Lunge[16] states that Classen(1) employed silicon as a catalyst in the contact process for making sulphur trioxide, and that Sulzberger[17] used nickel silicate reduced by hydrogen in which process nickel and silicon are said to be formed in the free state. In the present investigation the catalytic action of silicon was tested in a few cases which will be described later.

The investigations on the reducing action of silicon appear to have been limited largely to the oxides, the more important of these being: Cr_2O_3, CuO, Mn_3O_4, MnO_2, Fe_2O_3, Fe_3O_4, BaO_2, CaO, Ag_2O, Na_2O_2 and BaO_2 mixtures, PbO and CuO mixtures, $FeO.Cr_2O_3$, $FeO.WO_3$, TiO_2, Bi_2O_3, HgO, MoO_3 SnO_2. In addition to these, the reducing action of silicon on certain other compounds, such as: $PbCrO_4$, $K_2Cr_2O_7$, $PbSO_4$, has been studied.[18] Reports on investigations of this kind are not numerous, and, in some cases, are very general and incomplete. For example, H. N. Warren[19] states that "a large number" of metallic oxides when admixed with silicon become reduced when heated, but later he mentions only six specifically. He believed that he had obtained a lead silicide when litharge was reduced with an excess of silicon, but gives no indication as to why he drew this conclusion, except to say that "a brittle lead silicide is obtained as a regulus." He also states, merely, that with copper and all readily reducible oxides either a silicide is obtained, or, when the oxide is in excess, the pure metal is formed.

The special object of the present investigation was to attempt to use commercial crystalline silicon as a reducing agent for a series of inorganic compounds.

[15] Moissan, *l. c.*, 405.
[16] Sulphuric Acid and Alkali, 1, (1) supplement, 282.
[17] *Ibid.*, 283.
[18] Vigouroux, Compt. rend. (1895), 120, 367-70.
[19] H. N. Warren, *l. c.*, 75

A large number of reactions were tried in a preliminary way in order to determine what substances would react with silicon at all. From the mass of data so accumulated, a few promising reactions were selected and studied more in detail. Whenever feasible, the nature of the products formed was ascertained, so as to allow of a statement of the probable course of the reaction. Unfortunately, in many cases amorphous slags were formed, which, of course, were of the nature of solid solutions. In these the reduction products of the reaction were frequently dispersed in such extremely small globules that it was entirely impossible to isolate them and to determine their exact nature by means of chemical analysis. However, in some instances examination with the microscope did give a clue to the character of the products formed.

II. MATERIALS AND EXPERIMENTAL METHODS EMPLOYED.

1. *Materials.*

The silicon used was a commercial variety of crystalline silicon in lump form, obtained from the Carborundum Co., at Niagara Falls, N. Y. This material was powdered in a steel mortar until most of it would pass through a one-hundred mesh sieve. In order to separate the iron introduced from the mortar and pestle, the powder was boiled with concentrated hydrochloric acid for several hours, washed with water, and finally dried. When dry, the material was carefully mixed in order to secure homogeneity. It was then kept in stoppered bottles.

A systematic qualitative analysis of a ten gram sample showed the presence of iron and a trace of aluminum. Although this analysis was conducted in duplicate, no manganese, calcium or magnesium could be found. The residue remaining after treatment of the sample in a platinum crucible with nitro-hydrofluoric acid would consist of any carbon and silicon carbide which might be present, according to Albro,[20] who made use of this fact to determine the carbon and silicon carbide in an analysis of silicon compounds. A small amount of such a residue was found indicating the presence of carbon or silicon carbide, or both.

The total silicon content was determined by fusing the sample

[20] Trans. Am. Electrochemical Soc. (1907), **12**, 229-239.

in an iron crucible with sodium peroxide, separating the silicon as silicon dioxide, and determining its amount in the usual manner.

The iron in the silicon was determined by fusing the sample in a white porcelain crucible with sodium peroxide, transferring the cooled mass with water to a porcelain casserole, treating with concentrated hydrochloric acid to dissolve all of the iron and then determining the latter volumetrically by means of potassium dichromate.

The free silicon was determined by the method of Philips.[21] This method is based on the fact that an approximately thirty percent solution of KOH dissolves free silicon with the evolution of hydrogen. This gas is measured and the corresponding quantity of silicon calculated. The iron silicide is not attacked in this treatment with KOH.

The amounts of free carbon and of silicon carbide were determined by Albro's[22] rapid method, based on the fact that silicon and silicon dioxide are attacked by a mixture of concentrated nitric and hydrofluoric acid while graphitic carbon and silicon carbide remain unaltered.

The sample of silicon through 100 mesh was powdered in an agate mortar until it was fine enough to run through a bolting cloth sieve easily. Samples of this powder were used for analysis. The results are shown in Table I.

It is highly probable that all of the iron is present as $FeSi_2$, for, according to Hönigschmid[23] investigations of the various types of iron silicides present in technical ferrosilicon have shown that whenever ferrosilicons contain over fifty percent of silicon the only iron silicide found in the presence of the large excess of silicon is $FeSi_2$.

No free carbon was found in the sample; consequently the carbon present was combined with silicon as carbide. The amount of carbide was found to be 0.31 percent, and from this the amount of combined silicon would be 0.21, and the amount of combined carbon 0.10 percent.

[21] Zeit. angew. Chem. (1905), 18, 1969.
[22] Albro., *l. c.*
[23] *l. c.*, 221.

The various substances used in the reactions with silicon in this investigation were of c. p. grade of standard makes.

TABLE I.

Analyses of Powdered Silicon.

Ingredient	Sample Number I Percent	Sample Number II Percent	Sample Number III Percent	Mean Percent
Total silicon	95.07	95.16	94.68	94.97
Free silicon	90.10	90.23		
Total iron	4.90	4.89		4.90
Free carbon	0.00	0.00		0.00
Silicon carbide	0.30	0.30	0.34	
Total carbon (as calculated from silicon carbide)				0.10
Aluminum (trace)				
			Total	99.97

2. *Methods:*

Three different methods were employed in studying the reducing power of silicon toward other substances.

Method 1: The substance in question was mixed with silicon, both in a finely pulverized condition, and this mixture was then heated in a hard-glass test tube by means of an ordinary Bunsen burner. In a few instances the latter was replaced by a Méker burner, but whenever this was done it is specially mentioned below.

Method 2: The mixture of the finely divided substances was prepared as in Method 1, but in this case the mixture was placed in a Hessian crucible and the reaction started by means of an ignition cherry. This ignition cherry, similar to the one used in the Goldschmidt process, was made by mixing potassium chlorate and magnesium powder together with a little gelatine as a binder. The mass thus obtained was moulded into little balls each of which was provided with a piece of magnesium ribbon to act as a fuse.

Method 3: The finely pulverized reaction mixture, prepared as in Method 1, was placed in a Hessian crucible and the reaction started by means of an electric arc produced between electrodes made of the same sample of silicon from which the powder was

prepared. In each case a new pair of silicon electrodes was used, or, if the same electrodes were used a second time, they were first reground so as to remove any adhering material from previous reactions.

It was not an easy matter to prepare suitable slender pencil-like pieces of silicon for use as the electrodes between which the arc was formed. The silicon was available only in lump form. From these lumps pieces had to be knocked off, and then shaped by means of a carborundum wheel. The ordinary 110-volt lighting circuit was used in producing the arc. The distance between the silicon points was varied by hand, as required, to produce the desired effect. At times the silicon points fused together, but it was generally an easy matter to pull them apart. An alternating current ammeter placed in the circuit hardly ever registered more than eight amperes. From these facts it will be seen that the electric arc was used solely for the purpose of inducing the reaction by creating a high temperature locally, thus taking the place of the ignition cherry. The heat created by the arc was in no case sufficient to sustain the reaction. It is important to bear this in mind in considering the results tabulated below, for, of course, by this method no reactions were observed such as would take place if the entire mass were heated to a sufficiently high temperature. The mixture of lime and silicon, for instance, gave no reaction by Method 3, whereas, it is well known that when these substances are heated in an electric furnace reaction does take place. In some cases the reacting mixture was preheated with a Méker burner and then treated with the electric arc. Whenever this was done, it will be found specially indicated below.

Whenever it was possible to secure the reaction by means of Method (1), it was, of course, unnecessary to employ either of the other two methods. On the other hand, if Method (1) failed to give results and Method (2) was employed and caused the reaction to proceed, it was nevertheless deemed desirable also to use Method (3), because in the latter no foreign substances were introduced into the reacting mixture, since no ignition cherry was employed.

Indeed, the use of the electric arc between two silicon points (prepared from the same sample of silicon as that present in the reacting mixture itself) constitutes the unique part of this investi-

gation, and in no case has such an arc failed to cause the mixture to react if an ignition cherry (method 2) had induced the reaction. The arc induced the reaction in some cases in which the ignition cherry (Method 2) had failed. It is, therefore, clear that the electric arc is really the most efficient way of inducing the reaction, doubtless because of the high temperature which it creates locally.

III. TABULATION OF RESULTS OF PRELIMINARY EXPERIMENTATION.

At first molten KNO_3 was heated with pulverized silicon; oxygen was evolved but apparently no more rapidly than when KNO_3 was heated alone.

A mixture of $KClO_3$ and silicon was similarly heated and it was found that oxygen is evolved a little more rapidly than when the chlorate is heated alone. The contact action of silicon in the case of this reaction is consequently very slight.

Equal amounts of $KClO_3$ were mixed in turn with small amounts of well-dried SiO_2, Fe_3O_4, SiC, and crystalline silicon, each substance being introduced into a separate test tube containing the chlorate. These tubes were then heated on a sand bath at the same time by means of a Méker burner, the arrangement being such as to have the temperatures of the tubes approximately equal. The ease with which oxygen was given off was observed. The order of their effectiveness in facilitating the evolution of oxygen was as follows: Fe_3O_4, SiO_2, Si, SiC. The Fe_3O_4 increased the evolution of oxygen to such an extent that it could be readily noted. The other three substances, however, gave an effect that was quite slight, so that their catalytic power in decomposing molten potassium chlorate is hardly worthy of consideration.

TABLE II.

Effect Produced When Various Substances Mixed with Silicon are Treated According to Methods 1, 2 or 3.

The asterisk (*) indicates that the case so marked will be discussed in greater detail later. The mark (p) used in connection with some of the results obtained by method (3), indicates that the mixture was pre-heated with a Méker burner before treating with the arc. When proportions are given they mean simply proportions by weight, and not molecular proportions.

In some cases, like those of the sulphides, nitrates and carbonates heated with silicon, the compound suffered decomposition by heat, and if a reaction with silicon

TABLE II—*Continued.*

was noted, it was a reaction between these decomposition products and silicon, rather than between silicon and the original compound whose formula is mentioned.

No.	Substance	Method 1	Method 2	Method 3
1	Ag_2O	Some O_2 given off.	No marked action.	A strong reaction.*
2	$AgNO_3$	None.	None.	Slight reaction, products similar to those from No. 1.
3	Al_2O_3	None.	None.	None.
4	As_2O_3	Volatilized.	Volatilized.	Volatilized.
5	As_2O_5	Volatilized.	.....	Volatilized.
6	BaO_2	Vigorous reaction.	.....	.....
7	BaO	None.	None.	Reaction accompanied by a half-inch white, singing arc*
8	$BaSO_4$	None, even when Méker burner was used.	.....	None.
9	$BaCrO_4$	.....	Strong reaction.	Strong reaction.*
10	$BaMoO_4$	None.	.....	Very slight reaction (p).*
11	$BaWO_4$	.....	.....	Slight reaction (p).*
12	BaF_2	.....	.....	Very difficult to get even a slight reaction (p).
13	Bi_2O_3	Very slight reaction.	Very slight reaction.	Strong reaction, Bi globule.*
14	Bi_2S_3	None.	None.	Fairly rapid reactions, Bi globules.
15	H_3BO_3	None.	None.	None.†
16	$BeCO_3$	None.	.....	None.
17	CaO	None.	None.	None.
18	$CaBr_2$	None.	.....	None.‡
19	CaF_2	.....	None.	None.
20	$CaSO_4$	None.	None.	None.
21	$Ca(NO_3)_2$	None.	.....	None.
22	$Ca_3(PO_4)_2$	None.	.....	None.
23	$Ca(MnO_4)_2$	A slow glow, considerable heat liberated.	.....	.....
24	$CaCrO_4$	Slight reaction.	.....	Strong reaction (p).*
25	$CdCO_3$	.....	.....	Dense fumes of CdO. Some slag formed.
26	$Cd_{10}O_{13}$	None.	.....	None.
27	$Cd_{10}O_{17}$	None.	Some CdO formed.	.....
28	CdS	None.	.....	None.
29	Ce_2O_3	None.	.....	None.
30	CoO	None.	Fairly strong reaction.	Strong reaction.*
31	$CoCO_3$	None.	.....	Very slight. Some blue slag formed, also some black powder (CoO).
32	CuO	None.	Strong.	(p) Very strong reaction.*
33	$CuCO_3$	None.	.....	CuO formed first which was later reduced.
34	Cr_2O_3	None.	Slight reaction.	Good reaction.*

† Merely forms a glass with Si imbedded in it. ‡ The Ca flame was observed.

TABLE II—*Continued.*

No.	Substance	Method 1	Method 2	Method 3
35	Fe_2O_3	None.	Strong reaction.	.....
36	Fe_3O_4	None.	None.	None.
37	HgO	O_2 evolved.	None.	Strong reaction.*
38	HgS	None.	.....	SO_2 formed. No sudden reaction.
39	K_2CO_3	Slight, black puffy residue remaining.	None.	Strong reaction. Slag remaining. One inch singing arc, violet flame.
40	K_2CrO_4	None. Strong reaction, however, when the Méker burner was used.	.....	.....
41	$KClO_4$	Great evolution of O_2, but no explosion.	No explosion.	.....
42	$K_2S_2O_8$	Oxygen was given off as quickly as without the presence of the Si.	.....	.....
43	$KMnO_4$	Explosion on prolonged heating.	.....	.....
44	KIO_3	Oxygen liberated, no more readily than without the Si.	.....	.....
45	K_3AsO_4	None.	.....	A reaction, singing arc, black slag.
46	K_2MnO_4	None.	.....	A reaction, singing arc, black slag; reaction is very local.
47	$K_2Sb_2O_7$	Fairly strong reaction with much heat liberation at high temperature.	.....	.....
48	Li_2CO_3	Slight reaction.	.....	A strong lavender flaming arc, but the reaction would proceed only in the immediate neighborhood of the arc.
49	MgO	None.	None.	None.
50	MnO_2	Sudden glow at high temperature.	.....	A strong reaction, a large globule, surrounded by slag, formed.
51	MnO	.....	.....	None.
52	MnS	None.	.....	Reaction — first SO_2 fumes, then a fairly rapid reaction proceeding without the arc. A molten mass formed, a brittle material (slag) covered with a white material.
53	MoO_3	.....	.....	(p) Fairly good reaction, but it would not proceed in the absence of the arc.*

TABLE II—*Continued.*

No.	Substance	Method 1	Method 2	Method 3
54	Na_2O_2	Very violent reaction.	.....	.....
55	Na_2CrO_4	Strong reaction when Méker burner was used.	.....	.....*
56	CH_3COONa (fused)	None.	None.	A half-inch singing arc.
57	Na_2WO_4	Strong reaction when heated over the Méker burner.	.....	.....*
58	NiO (green)	None.	None.	A little black powder formed.
59	$NiCO_3$ (anhydrous)	When heated over a Méker burner a black powder formed.	.....	.....
60	$NiCl_2$	None.	.....	None.
61	Pb_2O	None.	.....	None, except a slight amount of a yellow and of a red deposit formed on the electrodes.*
62	PbO	Strong reaction.	Very strong reaction.	Strong reaction. A large globule of Pb formed, surrounded by slag.*
63	Pb_2O_3	.....	.....	Strong reaction. Small globules in a porous slag formed.*
64	Pb_3O_4	Very strong reaction.	.....	Violent reaction which started immediately. Lead globules formed surrounded by slag.*
65	PbO_2	On slight heating a violent reaction resulted, a white substance (SiO_2) formed together with lead globules.	Violent reaction.	Immediate reaction of a violent nature.*
66	$PbSO_4$	A glow at high temperatures.	.....	SO_2 fumes resulted. Reaction started soon, but would not proceed in the absence of the arc.*
67	$PbCrO_4$	Sudden reaction with heat and light evolution at high temperatures.	Strong reaction.	Strong reaction.*
68	$PbWO_4$	Reaction occurred when a Méker was used.	.....	A slowly spreading reaction, with the formation of slag.*
69	$PbMoO_4$	None.	.....	Slight reaction (p).*
70	$Pb(NO_3)_2$	Very slight reaction, NO_2 fumes.	Slight reaction. NO_2 fumes.	A good reaction, which proceeds without the arc. A black slag formed, no globules.
71	$PbCl_2$	None; substance volatilized.	.....	Slight reaction in the immediate neighborhood of the arc.*

TABLE II—*Continued.*

No.	Substance	Method 1	Method 2	Method 3
72	PbI_2	Iodine vapors. No reaction.	.....	I_2 vapors, yellow fumes of oxide, no reaction otherwise.
73	PbF_2	Mild reaction; similar to that with PbO.	.....	.....
74	$PbCO_3$	.....	Slow reaction.	Slow reaction, with white fumes.
75	PbS	.....	Strong reaction.	Action started after a time, SO_2 fumes, a lead globule formed.
76	$Pb(BO_2)_2$	None.	.....	Fairly rapid reaction, but quite local. A brittle black slag formed, but no globules.
77	$PbSiO_3$	None.	.....	.....
78	P_2O_5	None.	.....	.....
79	Sb_2O_3	None.	.....	Slow reaction, dense white fumes, metallic globules formed.*
80	Sb_2S_3	None.	Strong reaction.	First brown vapors formed, then a dense white vapor and a flaming ¾-inch singing arc resulted. A slight odor of SO_2 was noticed.
81	Sb (powder)	None.	.....	None. Mixture conducted the current well and became red hot, no globules.
82	SnO (black)	Slight glow.	Strong reaction.	Reduced to Sn; considerable yield of Sn.*
83	SnO_2 (white)	None.	.....	Very slight reduction in immediate neighborhood of the arc.
84	$SrCO_3$	None.	Slight reaction.	.....
85	SrO_2	Very strong reaction.	.....	.....
86	$Sr(NO_3)_2$	A few sparks, NO_2 fumes.	Slight reaction.	Did not react readily; a molten mass formed in neighborhood of the arc, hardening to a slag. Singing arc.
87	WO_3	.....	.....	Rather slow reaction similar to that with MoO_3 (p).*
88	ZnO	None.	A reaction occurred.	(p)—A very poor and very local reaction; no well defined product.
89	$ZnCl_2$	None.	.....	None. $ZnCl_2$ volatilized (p).
90	$ZnSO_4$	None.	.....	None.
91	ZnS	None.	None.	None, some SO_2 fumes.
92	$K_2Cr_2O_7$	.....	.....	Readily reduced to a porous dark green slag.

IV. RESULT OF REACTIONS STUDIED IN GREATER DETAIL.

1. *Lead Compounds.*

An examination of the tabulated results shows that many lead compounds react readily when heated with silicon, in some cases with violent action. Investigators[24] agree pretty generally that lead will dissolve silicon at high temperatures, but that it crystallizes out on cooling, as already pointed out. H. N. Warren states that although no silicide of lead forms when the elements are heated together, a brittle regulus of a lead silicide forms when an excess of silicon is heated with litharge, and further that when the litharge is in excess only metallic lead forms. The reaction, he says, takes place at once when the mixture of litharge, in excess, and silicon is heated to dull redness. This is the only statement found at variance with the generally accepted view that lead forms no silicides. Ladenburg[25] states that lead oxide and silicon give a silicate of lead with incandescence, and that with an excess of silicon a silicide of lead forms. This statement is undoubtedly founded on H. N. Warren's article.

(*a*) *Oxides of Lead.*

With the exception of Pb_2O, all the oxides of lead react readily with silicon when the mixture of the oxide and silicon is heated. The greater the oxygen content, the more violent the reaction, as the table above given shows.

Pb_2O: The theoretical equation,

$$2Pb_2O + Si = 4Pb + SiO_2,$$

would require a mixture of about 30 parts of Pb_2O to 1 of Si. It was found that a mixture of 34.3 parts of Pb_2O to 1 of Si would not react when heated with a Méker burner, or with the arc. It was found that a mixture of 5 parts of Pb_2O to 1 of Si, in which the Si is greatly in excess, also would not react. A little of the yellow oxide formed on the electrodes, but that was the only change observed. It was consequently concluded that Si will not reduce Pb_2O by the methods employed.

[24] Watts, *l. c.*; Moissan, *l. c.*, IV, 1034; Winkler, *l. c.*; S. Tamaru, Zeit. anorg. Chem. (1909), **61**, 40

[25] Handwörterbuch der Chemie, **10**, 733.

PbO: A mixture of silicon with this oxide reacted rapidly and strongly whether method 1, 2 or 3 was used. A slag and metallic lead resulted. When the proportions used were approximately those called for by the equation,

$$2PbO + Si = 2Pb + SiO_2,$$

a large globule of lead was found in the center of the cooled slag. When the proportions were reduced from 16 parts of PbO to 1 part Si, to 2 parts of PbO to 1 of Si, small globules were found dispersed throughout the slag. These were not at all brittle. They proved to be metallic lead.

Warren's statement that an excess of Si with litharge gives a brittle silicide of lead when heated is therefore not borne out by the experiments. Silicon easily reduces lead oxide, and the reaction probably is:

$$3PbO + Si = PbSiO_3 + 2Pb.$$

Pb_2O_3: A mixture of 11 parts of Pb_2O_3 and 1 part of Si, which is approximately the proportion called for by the equation,

$$2Pb_2O_3 + 3Si = 4Pb + 3SiO_2,$$

reacted when subjected to the arc, and the reaction, once started, proceeded in the absence of the arc. A lead silicate slag formed containing small globules of lead. Silicon therefore reduces Pb_2O_3 with the formation of lead and lead silicate, largely the latter. The reaction may be represented thus:

$$2Pb_2O_3 + 2Si = 2PbSiO_3 + 2Pb.$$

Pb_3O_4: A mixture of 12.2 parts of Pb_3O_4 and 1 part of Si, which is the proportion called for by the equation,

$$Pb_3O_4 + 2Si = 2SiO_2 + 3Pb,$$

ignited at once when a spark from the arc touched it. When to the molten mass more of the same mixture was added, it continued to react with about the speed of burning black gun powder. Lead globules, surrounded by slag of lead silicate, were formed. No silicide was observed. Mixtures containing various proportions of the ingredients when heated over a Bunsen flame (Method 1)

reacted with a sudden spurt of flame. Si consequently reduces Pb_3O_4 with violence, forming lead and lead silicate, probably according to the following equation:

$$3Pb_3O_4 + 4Si = 4PbSiO_3 + 5Pb.$$

PbO_2: Mixtures of PbO_2 and Si when heated over a Bunsen flame reacted violently on slight heating, and the evolution of heat was sufficient to melt the end of the test tube. A slag of lead silicate was formed together with globules of lead and a white powder, SiO_2, near the upper end of the test tube.

A mixture containing the proportions called for by the equation,

$$PbO_2 + Si = Pb + SiO_2.$$

when subjected to the arc, reacted at once with the formation of dense white fumes of SiO_2, and of a slag of lead silicate, in which globules of lead were embedded. Traces of the yellow and red oxides of lead also were noted.

The main reaction representing the reduction may be expressed thus:

$$3PbO_2 + 2Si = 2PbSiO_3 + Pb.$$

(*b*) *Lead Chloride.*

The literature gives no account of any investigation of the reaction between silicon and lead chloride. When a mixture of ten parts of $PbCl_2$ and 1 part of Si, corresponding to double the quantity of silicon required by the hypothetical equation,

$$2PbCl_2 + Si = SiCl_4 + 2Pb,$$

was subjected to the action of the arc, a slight reaction ensued in the immediate neighborhood of the arc. At the same time a dense, white cloud appeared, due to the volatilization of lead chloride. When a mixture was heated in the Bunsen flame, volatilization of lead chloride also occurred, but apparently no reaction. A slag of lead silicate was formed, but no silicide or globules of lead were observed. It is consequently probable that some silicon chloride was formed which, being volatile, would, of course, escape. The reaction may be represented thus:

$$2PbCl_2 + 3Si + 3O_2 = 2PbSiO_3 + SiCl_4.$$

(c) *Lead Sulphate.*

Vigouroux[26] states that amorphous silicon reduces $PbSO_4$, but he does not go into details.

A mixture of silicon and lead sulphate reacted quietly at high temperatures when heated over a Bunsen flame. When mixtures containing 6 parts or 7 parts of $PbSO_4$ to 1 of Si were treated with the arc, a reaction took place, but it would not continue in the absence of the arc. Gray fumes were formed and a strong odor of SO_2 was noticeable. Some small globules of lead were found. A small quantity of yellow lead oxide also was found around the edge of the crucible. On treating the residue with H_2SO_4, also on merely grinding it in the air, H_2S was evolved, showing the presence of a sulphide. It is, therefore, evident that a number of reactions go on simultaneously. The essential changes may be represented by the following equations:

$$PbSO_4 + Si = PbS + SiO_2$$

$$2PbS + 3O_2 = 2PbO + 2SO_2;\ PbO + SiO_2 = PbSiO_3;$$

$$3PbO + Si = 2Pb + PbSiO_3$$

A mixture containing 21.6 parts of $PbSO_4$ to 1 of Si, when treated with the arc, reacted with difficulty. With a smaller proportion of $PbSO_4$ the reaction proceeded with greater ease, as one would expect.

2. *Chromates, Tungstates and Molybdates.*

Chromium, tungsten and molybdenum are known to form silicides and consequently it was thought that at high temperatures silicon might react with chromates, tungstates and molybdates, possibly with the formation of silicides. A search through the literature revealed nothing to indicate that the reactions of silicon with chromates, tungstates and molybdates had ever been studied. There was no mention of such reactions, and the preparation of silicides by this means has evidently never been attempted. A possible exception is that Vigouroux[27] mentions that certain oxidizing agents such as $PbCrO_4$ and $K_2Cr_2O_7$ decompose with explosion and incandescence at red heat when heated with silicon.

[26] Compt. rend. (1895), 120, 367-70.

[27] Vigouroux, *l. c.*

The preliminary experiments already described showed that chromates are easily reduced by silicon and they also suggested the possibility of reactions between silicon and certain molybdates and tungstates with the possibility of obtaining silicides. The following were studied: Chromates of barium, calcium, sodium, and lead; molybdates of barium, and lead; tungstates of barium, sodium, and lead.

In each case the proportions were taken approximately as called for by a hypothetical equation according to which one of the products would be a silicide. Each one will now be taken up in detail.

The molybdates of barium and lead were prepared by precipitation, the calculated amount of ammonium molybdate in solution being added to a solution of barium chloride in one case, and one of lead acetate in the other. The resulting precipitates were thoroughly washed and then dried. Even if any traces of ammonium salts had remained as impurities they would have been volatilized at the temperatures attained in the experiments.

The tungstates were prepared from a solution of sodium tungstate by precipitation with the calculated amounts of lead acetate and barium chloride respectively. The products were washed carefully with distilled water and then dried.

(*a*). *Chromates.*

$BaCrO_4$: When a mixture of 2.6 parts of $BaCrO_4$ to 1 part of Si is ignited with an ignition cherry (Method 2) a strong reaction occurs. With the arc (Method 3) the reaction starts rapidly and then proceeds quietly, in the absence of the arc, forming a brittle, porous dark green slag containing a dark grey crystalline globule, composed of needle-like crystals.

This slag was found to contain barium and chromium. A qualitative test of the globule showed the presence of chromium, silicon and iron. No barium could be detected by means of the flame test, and no precipitate resulted when the dissolved melt obtained by fusing the globule with sodium peroxide was treated with sulphuric acid. The globule was not affected by acids or strong sodium hydroxide solution. These results indicate the presence of a silicide.

A quantitative analysis of this silicide gave the following results:

Ingredient	Sample Number I Percent	Sample Number II Percent	Mean Percent	
Total silicon	59.36	59.43	59.40	59.40
Free silicon	16.61	16.59	16.60	
∴ Combined silicon	.....	.....	42.80	
Chromium	34.44	34.15	34.30	34.30
Iron	5.67	5.77	5.72	5.72
		Total		99.42

Assuming that the iron is present as $FeSi_2$ only, the silicon combined with it is 5.80 percent of the sample. This leaves the silicon combined with the chromium 42.80 — 5.80, or 37.00 percent of the sample, whence the composition of the chromium silicide is 48.06 percent Cr and 51.94 percent Si. The following silicides of chromium have been described in the literature:[28]

Formula	Percent Cr	Percent Si
Cr_3Si	84.64	15.36
Cr_2Si	78.61	21.39
$CrSi_2$	47.88	52.12
Cr_3Si_2	73.38	26.62

It thus appears that the silicide formed in the reduction of the barium chromate is very likely $CrSi_2$.

The barium and some of the chromium of the chromate go into the slag forming silicates. To represent the entire chemical change by means of one equation would be rather cumbersome. Suffice it here to say that the products formed are $CrSi_2$ and a slag which consists of a mixture of the silicates of barium and chromium.

$CaCrO_4$: This compound was prepared from a solution of Na_2CrO_4 by precipitation with $CaCl_2$. The dry salt was mixed

[28] Hönigschmid, *l. c.*, 188; Watts, *l. c.*

with silicon, approximately in the proportion called for by the equation,

$$2CaCrO_4 + 7Si = 2CrSi_2 + 2CaSiO_3 + SiO_2.$$

The mixture, previously heated over the Méker burner, was subjected to the arc, when a good reaction resulted. A jet-black, glassy slag was obtained, with grey, brittle globules of a silicide resembling $CrSi_2$ scattered throughout and a large globule in the center of the mass. The globules were freed from the surrounding siliceous slag and analyzed. The results are shown in the following table:

Ingredient	Sample Number			Mean Percent	
	I Percent	II Percent	III Percent		
Total silicon	68.49	68.54		68.52	68.52
Free silicon	33.91	33.85	33.77	33.84	
∴ Combined Si	.....	.....	.....	34.68	
Chromium	26.74	26.76		26.75	26.75
Iron	4.05	4.15	4.00	4.07	4.07
		Total			99.34

Assuming that the iron is present only as $FeSi_2$, the silicon combined with it is 4.13 percent of the sample. This leaves the silicon combined with chromium 34.68 — 4.13, or 30.55 percent of the sample. The percentage composition of the silicide formed is Cr 46.68 and Si 53.32. Therefore the silicide formed is undoubtedly $CrSi_2$.

Calcium chromate therefore reacts well with silicon at relatively high temperatures, and $CrSi_2$ is formed when approximately the proportions called for by the equation,

$$2CaCrO_4 + 7Si = 2CrSi_2 + 2CaSiO_3 + SiO_2,$$

are used. This equation represents substantially what takes place.

$PbCrO_4$: Vigouroux,[29] in discussing the reactions between amorphous silicon and certain oxides and oxidizing agents, states that when $PbCrO_4$ and amorphous silicon are mixed and heated to red heat, a reaction of an explosive character accompanied by

[29] *l. c.*

incandescence takes place, but he does not go into detail concerning this reaction. He states in the course of the article that amorphous silicon resembles crystalline silicon in most of its properties.

In the present investigation it was found that a mixture of crystalline silicon and fused $PbCrO_4$, when heated to a high temperature in a test tube, will react suddenly with the evolution of heat and light. By the use of Method 2 a strong reaction was also brought about.

A mixture of 23 parts of $PbCrO_4$ and 1 of Si (containing then a great excess of $PbCrO_4$) was treated with the arc. The reaction started with difficulty and continued slowly in the absence of the arc, until all of the material had reacted. A dark green, hard, brittle slag formed, but no globules of a metal or of a silicide. A slight amount of PbO formed.

When the proportions used were 6 parts of $PbCrO_4$ to 1 of Si the reaction started with ease and proceeded rapidly and spontaneously, forming a brittle, dark green slag. No globules of lead or of a silicide were formed.

When the proportions used were 3 parts of $PbCrO_4$ to 1 of Si the results were the same as in the last case, though here the Si was in excess.

The products obtained in all cases were the same as far as could be ascertained by qualitative tests. They were found to contain both lead and chromium. An analysis of the product formed when 6 parts of $PbCrO_4$ and 1 of Si reacted gave results as follows:

Ingredient	Sample Number			Mean Percent	
	I Percent	II Percent	III Percent		
Total silicon	14.78	14.72		14.75	14.75
Free silicon	6.23	6.04		6.14	
∴ Combined silicon	.....	.....	.....	8.61	
Chromium	19.64	19.88	19.67	19.73	19.73
Iron	1.45	1.39	1.56	1.47	1.47
Lead	51.91	51.77		51.84	51.84
Oxygen (by difference)	.....	.....	.....	.....	12.21
			Total		100.00

However, from the results of the analysis it was clearly not possible to arrive at any conclusion as to the individual compounds present. This slag is doubtless of the nature of a solid solution, being a complex mixture of the silicates of the metals present. Any attempts to write equations as to the reactions that occur would therefore be merely speculative in character, and hence are omitted in this case. Suffice it here to say that no silicides were formed and that no free metal was found in the reaction products.

Na_2CrO_4: The theoretical reaction,

$$2Na_2CrO_4 + 7Si = 2CrSi_2 + 2Na_2SiO_3 + SiO_2,$$

requires that Na_2CrO_4 and Si be present in the proportions of 1.6 parts of Na_2CrO_4 to 1 of Si. The proportions used were 2 parts of Na_2CrO_4 to 1 of Si, so that Na_2CrO_4 was in excess of the requirements. The mixture when heated over a Méker burner reacted strongly as soon as the water of crystallization had been driven off. A large globule, resembling $CrSi_2$, was formed, surrounded by a black slag which was light green on the surface exposed to the air. Throughout this slag were dispersed smaller globules of the silicide. The globule was analyzed with the following results:

Ingredient	Sample Number I Percent	Sample Number II Percent	Mean Percent	
Total silicon	66.98	66.55	66.76	66.76
Free silicon	29.61	29.57	29.59	
∴ Combined Si	.....	.....	37.17	
Chromium	29.15	29.00	29.08	29.08
Iron	4.10	4.07	4.09	4.09
		Total		99.93

Assuming that the iron is present as $FeSi_2$ only, the silicon combined with it is 4.15 percent of the sample. This leaves the silicon combined with chromium 37.17 — 4.15 or 33.02 percent of the sample. The percentage composition of the silicide formed is therefore Cr 46.83 and Si 53.17. Therefore the silicide formed is undoubtedly $CrSi_2$.

Sodium chromate, then, reacts very well with silicon at elevated temperatures, and $CrSi_2$ is formed when an excess of Na_2CrO_4 over the amount called for by the equation,

$$2Na_2CrO_4 + 7Si = 2CrSi_2 + 2Na_2SiO_3 + SiO_2,$$

is used. This equation represents substantially what takes place.

(*b*) *Molybdates.*

$BaMoO_4$: A mixture of approximately 3 parts of $BaMoO_4$ to 1 of Si was used in which the Si is somewhat in excess of the amount required by the equation,

$$6BaMoO_4 + 18Si = 6BaSiO_3 + 3Mo_2Si_3 + 3SiO_2.$$

When this mixture was treated with the electric arc (Method 3), after having been preheated over a Méker burner, a very slight amount of slag formed in the immediate neighborhood of the arc. No globules of a metal or of a silicide were formed. The slag itself was a complex amorphous glass being a mixture of the silicates of barium and molybdenum.

$PbMoO_4$: A mixture of approximately 5 parts of $PbMoO_4$ to 1 of Si was used as the reaction mixture, the $PbMoO_4$ being therefore very slightly in excess of the quantity called for by the hypothetical equation,

$$3PbMoO_4 + 8Si + 3O_2 = 3PbSiO_3 + MoSi_2 + Mo_2(SiO_3)_3.$$

This mixture was heated by means of the arc (Method 3) after first preheating over a Méker burner. A reaction started rather quickly, but it proceeded only in the immediate neighborhood of the arc. A hard, brittle, homogeneous, gray mass formed. No globules of a metal or of a silicate were formed. The mass was undoubtedly a complex mixture of silicates of lead and molybdenum. It is well known that molybdenum forms various complex compounds. It is, therefore, not feasible to attempt here to represent the reaction by means of an equation, and since there was no possibility of isolating the individual products from the final mass, a definite equation representing the course of the reaction can not be written.

(*c*) *Tungstates.*

$BaWO_4$: A mixture of 5 parts of $BaWO_4$ and 1 part of Si containing approximately the proportions called for by the hypothetical equation,

$$4BaWO_4 + 11Si + O_2 = W_2Si_3 + BaSi_2 + 3BaSiO_3 + W_2(SiO_3)_3.$$

was used as the reaction mixture. This was treated with the electric arc (Method 3) after having been preheated over the Méker burner. A reaction took place. A very hard, porous slag was formed which contained one or two very small, brittle globules that adhered tenaciously to the slag. These globules were not attacked by HCl or HNO_3, and only very slightly by hot concentrated NaOH solution. They were, therefore, not barium silicide, nor were they globules of lead. They resembled the silicides of tungsten (W_2Si_3 and WSi_2) in their resistance to the action of mineral acids. Because of the very small amount of silicide formed, it was not possible to analyze it quantitatively.

In summary, then, it appears that a slight amount of a silicide of tungsten is formed in the reaction. There was no evidence that the silicide of barium was formed, and the slag was doubtless a mixture of silicates of barium and tungsten.

$PbWO_4$: A mixture of 6.5 parts of $PbWO_4$ to 1 of Si, in which the proportions are approximately those required by the theoretical equation,

$$4PbWO_4 + 10Si + 5O = 4PbSiO_3 + W_2(SiO_3)_3 + W_2Si_3,$$

was prepared. When this mixture was heated over a Méker burner a reaction resulted. When the arc (Method 3) was used, a reaction also occurred spreading slowly throughout the mixture and resulting in a hard, grey, sintered mass. No globules of metal or of a silicide were observed.

The powdered material was only slightly affected by aqua regia. Hot concentrated caustic soda acted slightly upon it, doubtless because of the presence of an excess of silicon. The product was probably a mixture of silicates of lead and tungsten, together with some free silicon.

Na_2WO_4: A mixture of Na_2WO_4 and Si containing approximately the proportions required by the hypothetical equation,

$$2Na_2WO_4 + 6Si = W_2Si_3 + 2Na_2SiO_3 + SiO_2,$$

was heated over a Méker burner. After a time a strong reaction took place. A flame shot out of the crucible, due, no doubt, to the formation of hydrogen by the interaction of silicon and the remaining water of crystallization. The mass became incandescent, and white fumes, apparently of silica, were observed. The residue was of a dull black hue, readily pulverizable, and hard enough to scratch glass easily. No globules of a metal or of a silicide were formed.

On heating the product with distilled water, an inflammable gas (hydrogen) was evolved in considerable amount, which fact will be investigated separately later. On treatment with hot concentrated NaOH, hydrogen was copiously evolved. In the latter respect the material acts like silicon. When a suspension of crystalline silicon, however, is heated to boiling with distilled water, no hydrogen is evolved, as is well known. Common acids, HCl, HNO_3, aqua regia, H_2SO_4 did not affect the product noticeably. It would be difficult to express the reaction which took place by an equation. What is definitely known is that no globules of a silicide are formed, and also no metallic globules. The hard sintered mass contains free silicon which is imbedded in what is doubtless a complex mixture of the silicates of sodium and tungsten.

3. *Miscellaneous Compounds.*

Cr_2O_3: Both Watts[30] and Hönigschmid[31] give summaries of the work that has been done on the chromium silicides. They describe four silicides, namely, Cr_3Si, Cr_2Si, $CrSi_2$, Cr_3Si_2, but there is no record that any definite silicide of chromium was ever prepared by reduction of Cr_2O_3 by elementary, crystalline silicon.

B. Neuman,[32] in discussing the reduction of oxides of some of the high melting metals by means of silicon, states that it is difficult to obtain chromium when less than seven percent of silicon is used in the reaction mixture.

[30] *l. c.,* 262.
[31] *l. c.,* 188.
[32] *l. c.,* 169-172.

H. Goldschmidt[33] states that silicon alone will not react with Cr_2O_3.

H. N. Warren[34] mentions the reduction of chromium oxide by silicon. Presumably he means chromium sesqui-oxide, Cr_2O_3.

In the present research it was attempted to secure a reaction between Cr_2O_3 and crystalline silicon. Method 3 was the only one which gave a positive result. A mixture of 3 parts of Cr_2O_3 and 1 of Si corresponding approximately to the equation,

$$2Cr_2O_3 + 3Si = 4Cr + 3SiO_2,$$

with somewhat of an excess of silicon, was used. It was rather difficult to get the reaction to proceed. A dark green, almost black, slag resulted with many small globules of what appeared to be a silicide scattered throughout the mass. Some of these globules were collected, mechanically freed as much as possible from the adhering slag, and subjected to analysis with the following results:

Ingredient	Sample Number I Percent	Sample Number II Percent	Mean Percent	
Total silicon	59.79	59.66	59.73	59.73
Free silicon	29.40	29.46	29.43	
Combined silicon	.....	.....	30.30	
Chromium	30.41	30.59	30.50	30.50
Iron	5.04	5.14	5.09	5.09
Oxygen in adhering slag (by difference)	.....	.....	4.58	4.68
	Total			100.00

Assuming that the iron is present as $FeSi_2$ only, the silicon combined with it is 5.16 percent of the sample. This leaves the silicon combined with the chromium 30.30 — 5.16 or 25.14 percent of the sample. This is, however, not all combined with chromium as a silicide, for it was impossible to remove all of the adhering slag from the globules of the silicide before analysis, and so a silicate is known to be present. From the percent of oxygen present in the sample it was calculated that a slag was present which contained

[33] Zeit. Elektrochem (1908), **14**, 558.

[34] *l. c.*

oxygen equal to 4.68 percent of the sample, silicon 2.76 of the sample, and chromium 3.38, assumed to be combined as $Cr_2(SiO_3)_3$. From these considerations it will be seen that the silicide contains chromium to the amount of 30.50 — 3.38 or 27.12 percent of the sample, and silicon to the extent of 30.30 — (5.16 + 2.76), or 22.38 percent of the sample. The percentage composition of the silicide is therefore, chromium 54.79, and silicon 45.21. This percentage composition corresponds to the formula Cr_2Si_3.

As has been stated before,[35] the following silicides of chromium are recognized by writers who have collected the results of various investigations: Cr_3Si, Cr_2Si, $CrSi_2$, Cr_3Si_2. None of these correspond to the formula deduced for the chromium silicide under discussion at present. Frilley[36] claims, from a study of chromium-silicon alloys, that his results show the existence of the following chromium silicides: Cr_2Si, $CrSi_2$, Cr_3Si, $CrSi$, Cr_2Si_3, and Cr_2Si_7.

The entire experiment was repeated to determine if the results could be duplicated. The resulting globules of the silicide were freed from the adhering slag as much as possible mechanically and analyzed with the following results:

Ingredient	Sample Number I Percent	Sample Number II Percent	Mean Percent	
Total silicon	63.37	63.48	63.43	63.43
Free silicon	36.42	36.30	36.36	
∴ Combined silicon			27.07	
Chromium	25.67	25.74	25.70	25.70
Iron	4.40	4.31	4.36	4.36
Oxygen in slag (by difference)			6.51	6.51
Total				100.00

The percentage composition of the chromium silicide was determined in the same way as before and was found to be, chromium 52.74 and silicon 47.26.

The theoretical percentage composition of Cr_2Si_3 is 55.06 Cr, and 44.94 Si. The analysis of the silicide found in the first trial

[35] Hönigschmid, *l. c.*, 188; Watts, *l. c.*

[36] Gmelin, Kraut, Handbuch d. anorg. Chem., 3, (1), 1392; Frilley, Rev. Metal (1911), 8, 476.

yielded 54.79 Cr and 45.21 Si. The second entirely independent trial just described yielded a silicide containing 52.74 Cr, and 47.26 Si. From these data (which are quite as concordant as one could very well expect when the nature of the experimental problem is considered) it is highly probable that the silicide formed is Cr_2Si_3. This is also precisely what one would naturally expect when Cr_2O_3 is reduced. To be sure, it was assumed in these considerations that the chromium silicate simultaneously formed has the composition $Cr_2(SiO_3)_3$. References to chromium silicate rarely occur in the literature. Moissan[37] refers to a natural chromium silicate, Wolkonskoite, which is found in Russia. The dark green slag, however, doubtless contains trivalent chromium, and so it seems reasonable to assume the presence of $Cr_2(SiO_3)_3$. The reaction might be represented by an equation as follows:

$$3Cr_2O_3 + 9Si = 2Cr_2Si_3 + Cr_2(SiO_3)_3.$$

There was no evidence that any of the oxide of chromium was reduced to metallic chromium.

WO_3: Vigouroux[38] melted a mixture of 100 grams of WO_3 and 230 grams of Si, and obtained W_2Si_3. Neuman[39] claims to have reduced WO_3, and to have obtained tungsten containing 2.26 percent of Si or less, by the use of Si in the presence of equal parts of CaO and Al_2O_3. H. N. Warren[40] also states that silicon will reduce tungstic oxide when heated.

When a mixture of 5 parts of WO_3 to 1 of Si, corresponding approximately to the amounts called for by the hypothetical equation,

$$3WO_3 + 5Si = WSi_2 + W_2(SiO_3)_3,$$

was treated with the arc (Method 3), after having been preheated over a Méker burner, a slow local reaction occurred and a slight amount of a hard slag formed, but no tungsten or particles of a silicide. The addition of Na_2O_2 to the mixture to bring about a violent reaction and a high temperature also did not affect the final outcome. Furthermore, adding PbO_2 to produce a more intense reaction merely caused a slow reaction to take place and

[37] Moissan, *l. c.*, **4**, 639.
[38] Vigouroux, Compt. rend. (1898), **127**, 393
[39] *l. c.*
[40] *l. c.*

yielded a sintered mass, without, however, forming tungsten, or a silicide. The experiments performed consequently show that one cannot secure the metal or a silicide by the methods employed. The slight amount of amorphous slag, which was formed when the mixture of silicon and WO_3 was treated with the electric arc as described was undoubtedly a silicate of tungsten.

Since there was but a slight amount of this slag, and since there was no way of freeing it from adhering impurities, a quantitative analysis of the material was not made.

MoO_3: Vigouroux[41] reduced a mixture of MoO_2 and MoO_3 and Si (2½ parts of oxide to 1 of Si) in the electric furnace, and obtained Mo_2Si_3.

Neuman[42] states that he obtained molybdenum by the reduction of the oxide with silicon in the electric furnace, but that the product was contaminated with silicon.

H. N. Warren[43] also mentions the reduction of molybdenum oxide by silicon.

When a mixture of 2 parts of MoO_3 to 1 part of Si corresponding approximately to the requirements of the hypothetical equation,

$$8MoO_3 + 18Si + 3O_2 = 2Mo_2Si_3 + 2Mo_2(SiO_3)_3 + 6SiO_2,$$

was subjected to the arc (Method 3) after having been preheated over a Méker burner, only a very local reaction resulted. Dense black fumes of Mo_2O_3 appeared and a sintered mass formed, together with a slight quantity of white, feathery, needle-like crystals of MoO_3 which appeared on the electrodes. The sintered mass was hard, but not very cohesive. Similar results were obtained when the proportions used were 10 parts of MoO_3 to 1 part of Si.

When some litharge was added to the mixture of 2 parts MoO_3 and 1 part of Si in order to facilitate the reaction, and the mixture then heated over the Méker burner, a slow reaction took place with the formation of lead globules embedded in a hard, sintered mass. The addition of Na_2O_2 instead of PbO to facilitate the reaction also did not result in the formation of the metal or globules of a silicide.

[41] Vigouroux, Compt. rend. (1899), 129, 1238.
[42] Neuman, *l. c.*
[43] Warren, *l. c.*

The white crystals mentioned above were MoO_3. They were insoluble in water, lighter than the hard slag, and soluble in NaOH solution. The silicides of molybdenum, Mo_2Si_3 and $MoSi_2$, are not much affected by alkali solutions.[44]

When some of the product was allowed to stand in contact with water, a blue solution formed. This does not happen when molybdic acid is similarly treated. On withdrawing some of this blue solution from contact with the reduction product and allowing the liquid to stand in an open beaker, it gradually changed color, becoming in turn green, greenish yellow, and finally colorless. The blue solution, therefore, contained reduction products of MoO_3. The blue color remained unaffected by ordinary mineral acids except HNO_3, which destroyed the color because of oxidation. Solutions of NaOH and NH_4OH also had no effect on the blue solution, as one would expect.

In summary, then, MoO_3 is reduced to lower oxidation products, but not to metal when treated with Si as here described.

Sb_2O_3: Antimony forms no silicides.[45] No statements contradicting the above were found in the literature, and nothing was found to show that the question of the possibility of a reaction between silicon and Sb_2O_3 has ever been investigated.

A mixture of 7 parts of Sb_2O_3 and 1 of Si containing the Si in considerable excess above the amount required by the theoretical equation,

$$3Sb_2O_3 + 3Si = 4Sb + Sb_2(SiO_3)_3,$$

was treated with the arc (Method 3), and was found to react with difficulty. A black molten mass was formed in which a few very small globules of antimony were found imbedded in a black slag. This black slag was amorphous, being undoubtedly of the nature of a solid solution of silicates containing some free silicon in suspension. One may represent the essential features of the reaction by means of the following equation:

$$3Sb_2O_3 + 3Si = 4Sb + Sb_2(SiO_3)_3.$$

CoO: No record of an attempt to reduce CoO with silicon was found. Both Watts[45] and Hönigschmid[46] describe three silicides

[44] Hönigschmid, *l. c.*, 194
[45] Watts, *l. c.* 262.
[46] *l. c.*, 224.

of cobalt none of which were obtained by treatment of a mixture of silicon and cobalt oxide. The silicides they mention have the formulas, Co_2Si, $CoSi_2$, and $CoSi$.

A mixture of CoO and Si in approximately the proportions called for by the hypothetical equation,

$$6CoO + 10Si = 4CoSi_2 + 2CoSiO_3,$$

was treated with the electric arc (Method 3). A fairly strong local reaction occurred. A purple slag was formed in which were imbedded a large number of globules resembling a silicide. The reaction would not proceed in the absence of the arc.

The globules were freed mechanically from the adhering slag, but it was not possible to remove all of the slag in this manner. The globules had a crystalline fracture, although some were not brittle. Some of the globules were magnetic, others not. The magnetic globules were malleable and were attacked by HNO_3, but not by HCl or by alkali solution.

CoO, therefore, had been reduced by silicon with the formation of an amorphous silicate slag and one or more cobalt silicides, together with some metallic cobalt. Because of the impossibility of removing the adhering slag, the non-magnetic globules could not be obtained pure enough for a quantitative analysis. However, an indication that the non-magnetic globules were of the nature of a silicide was secured by a partial analysis which showed a total silicon content of 54.63 (mean of 54.62 and 54.64) percent. The following reaction represents substantially what took place:

$$9CoO + 11Si = 2Co + 4CoSi_2 + 3CoSiO_3.$$

CuO: Warren[47] merely mentions that copper oxide is reduced by silicon.

H. Goldschmidt[48] states that silicon reacts with copper oxide in the silico-thermic process, but that it does not give "good metal." The latter result is to be expected in view of the tendency of copper to form silicides.

Hönigschmid[49] gives the history of the work done on the two silicides of copper, Cu_2Si and Cu_4Si and observes that Labeau's careful studies have shown Cu_4Si to be the only silicide of copper.

[47] *l. c.*
[48] Zeit. Elektrochem. (1908), **14**, 558.
[49] *l. c.*, 151.

Watts[50] gives as the existing silicides of copper the same two, Cu_2Si and Cu_4Si, both of which were obtained by the use of copper in the electric furnace.

Rudolf,[51] however, claims that a thermal analysis shows that only two definite compounds of silicon and copper exist, namely, Cu_3Si and $Cu_{19}Si_4$, and recommends that the formulas, Cu_2Si and Cu_4Si be stricken from the literature.

The hypothetical equation,

$$3CuO + 2Si = CuSiO_3 + Cu_2Si,$$

calls for approximately 4.2 parts of CuO to 1 part of Si. Such a mixture was made, and strongly heated over a Méker burner, but no reaction occurred. While still hot the mixture was subjected to the action of the electric arc (Method 3) and a violent reaction took place. A molten mass formed near the electrodes. A large, brittle globule of a silvery white appearance was found at the center of a brittle, copper-colored slag throughout which smaller globules of the same material were scattered. No metallic copper was found.

The fractured globule showed a crystalline structure and became bronze colored within a short time. In this respect it resembles Cu_4Si.[52] The large globule was separated easily and completely from the surrounding slag. An analysis of this globule gave the following results:

Ingredient	Sample Number I Percent	Sample Number II Percent	Mean Percent	
Total silicon	12.14	12.51	12.32	12.32
Free silicon	0.40	0.38	0.39	
∴ Combined silicon	.....	.....	11.93	
Iron	2.49	2.40	2.45	2.45
Copper (by difference)	.....	.....	85.23	85.23
		Total		100.00

Assuming that the iron is present as $FeSi_2$ only, the silicon combined with it is 2.48 percent of the sample. This leaves the

[50] *l. c.*, 262.
[51] Zeit. anorg. Chem. (1907), 53, 216.
[52] Hönigschmid, *l. c.*, 157.

silicon combined with copper 11.93—2.48, or 9.45 percent of the sample. The percentage composition of the silicide formed is therefore, Cu 90.02, and Si 9.98. The percentage composition of Cu_4Si is, Cu 89.99, and Si 10.01. The globule was, therefore, Cu_4Si. The slag formed is undoubtedly a copper silicate. The reaction may be represented by the following equation:

$$6CuO + 3Si = Cu_4Si + 2CuSiO_3.$$

Ag_2O: There is disagreement in the literature as to the existence of silver silicide. G. de Chalmot[53] claims to have prepared a silicide of silver by subjecting a mixture of sand, charcoal, lime and pieces of silver to a current of 240 amperes, at 25 volts. He describes the silicide as being grey in color, rather tough, yet hard enough to scratch glass. By boiling it with nitric acid ($1HNO_3 + 2H_2O$) for 75 minutes only a part of the silver was dissolved, while SiO_2 was formed.

H. N. Warren[54] claims to have obtained a silicide of silver on heating a mixture of K_2SiF_6, metallic sodium, and amorphous silver. He states that silicon possesses "no considerable affinity toward either gold or silver except when in a nascent state, still that affinity appears to be considerably enhanced by combining with either metal when in the fused state a small quantity of an already prepared silicide." For example, some silver silicide is dissolved in the molten metal and the percentage of silicon can be raised by introducing some elementary silicon. Warren[55] also mentions an experiment in which silicon and silver oxide are projected into a red hot crucible with resulting incandescence and the formation of a semi-fluid mass containing about 40 percent silicon, which he refers to as "a curious compound."

Abegg[56] states that no well-defined compound of silver and silicon has been found. Ladenburg[57] merely quotes the result of Warren's experiment.[55] Moissan[58] states that silicon does not combine with silver, but is dissolved in it, and separates out on cooling. That silver forms no silicide is the commonly accepted view.[59]

[53] Am. Chem. Jour. (1896), **18**, 95.
[54] Chem News (1893), **67**, 303.
[55] Chem. News (1891), **64**, 75.
[56] Handbuch d. anorg. Chem., **11**, (1), 674.
[57] *l. c.*, 734.
[58] Compt. rend., **121**, 625-6. 1895.
[59] Watts, *l. c.*, 259; Hönigschmid, *l c.*

Silver oxide and silicon were mixed in the proportions of 7.5 parts of Ag_2O to 1 of Si. The Si was therefore greatly in excess of the amount required by the theoretical reaction,

$$2Ag_2O + Si = SiO_2 + 4Ag.$$

This mixture was treated with the arc (Method 3) and a strong reaction ensued. When the proportions were 10 parts of Ag_2O to 1 of Si the reaction was even stronger, and with 12 parts of Ag_2O to 1 of Si, it was very strong. In all of these cases the product consisted mostly of a light brown mass of no great coherence which contained small globules of silver, and was underlain by a thin, flat layer of metallic silver.

A qualitative test proved that the brown material contains oxygen which it gives off on heating. It was, therefore, an oxide of silver. The metal was silver. When the product of the reaction was heated with acids, a black residue, silicon, mixed with particles of silica, remained.

The product of the reaction was heated with HNO_3 for three hours to remove the Ag and silver oxide. The carefully washed and dried residue was tested as follows: A sample was subjected to the blow-pipe test and silver was found to be absent. The residue was found to be of about the same specific gravity as a Thoulet's solution of specific gravity nearly 3, thus indicating further that no silver compound was present in any quantity. This residue was therefore merely a mixture of silicon and silica.

The reaction consequently may be represented by the equation,

$$2Ag_2O + Si = SiO_2 + 4Ag.$$

It was found that no silicide could be obtained by the method employed, thus strengthening the view that a silicide of silver does not exist.

HgO: No mention of a silicide of mercury was found in the literature except a statement by Warren,[60] who says that the existence of mercury silicide is doubtful. The attempt was here made to get silicon and mercury oxide to react. On repeated trials it was found that neither Method 1 nor Method 2 produced any reaction with Si. However, with the aid of the arc (Method 3), a reaction was produced rather quickly. In one case

[60] Chem. News (1893), **67**, 303.

a mixture of 7 1/3 parts HgO to 1 part of Si was used, and in another case 6½ parts of HgO to 1 part of Si were used as a reaction mixture. These mixtures reacted with ease and the reaction was accompanied by showers of white particles of SiO_2.

Some of this material was collected. Besides SiO_2 it contained mercury, for by shaking some of it in a test tube, globules of mercury collected in the bottom of the tube. Also when some of the residue of the white particles which remained in the crucible and on the electrodes was ground in a mortar, mercury separated out.

It appears, therefore, that HgO can be reduced by Si at sufficiently elevated temperatures, but not at lower temperatures. At lower temperatures oxygen is simply evolved and the silicon is not attacked. The reaction at high temperatures may be represented by the equation,

$$2HgO + Si = 2Hg + SiO_2.$$

Bi_2O_3: No record of any attempt to reduce bismuth trioxide by means of silicon was found. Bismuth and silicon do not unite to form a silicide, but silicon dissolves in molten bismuth and crystallizes out on cooling.[61]

The attempt was here made to reduce Bi_2O_3 with Si in a mixture containing approximately the proportions called for by the equation,

$$2Bi_2O_3 + 3Si = 4Bi + 3SiO_2.$$

Reduction took place quickly when this mixture was treated with the electric arc (Method 3), forming a slag throughout which were scattered numerous globules of metallic bismuth. No silicide was observed. The reaction may, therefore, be represented by the equation,

$$3Bi_2O_3 + 3Si = 4Bi + Bi_2(SiO_3)_3.$$

BaO: Goldschmidt [62] reduced barium oxide by means of silicon in the electric furnace and obtained small amounts of barium silicide, $BaSi_2$.

[61] Gmelin-Kraut, *l. c.*, 3 (2), 945; Vigouroux, Compt. rend. (1896), **123**, 115; Watts, *l. c.*, 259.

[62] Zeit. Elektrochem. (1908), **14**, 558.

When mixtures of BaO and Si were treated by Methods 1 and 2, no reaction took place. However, when the electric arc (Method 3) was used a reaction took place. The reaction mixture used was 11 of BaO to 1 of Si, corresponding approximately to the proportions required by the hypothetical equation,

$$2BaO + Si = 2Ba + SiO_2.$$

A blinding white arc, ½ inch (1.2 cm.) long, formed, and a pale-green, powdery residue remained in the crucible, together with a very slight quantity of a white amorphous mass, which formed in the immediate neighborhood of the arc. No silicide or metal was formed. The slag probably contains silicates of barium, and the reaction may be represented by the equation,

$$BaO + Si + O_2 = BaSiO_3.$$

SnO: Vigouroux[63] states that amorphous silicon reduces tin oxide at rather low temperatures. In the present investigation a mixture of SnO and Si in the proportions called for by the equation,

$$2SnO + Si = 2Sn + SiO_2,$$

was used. This mixture, when heated over a Méker burner, reacted quietly, a good yield of metallic tin being obtained. This reaction is therefore,

$$2SnO + Si = 2Sn + SiO_2,$$

and it takes place when crystalline silicon is used as well as when the amorphous silicon is employed as in Vigouroux's experiments.

By substituting SnO_2 instead of SnO no notable reaction resulted by either Methods 1 or 3.

V. GENERAL SUMMARY.

1. Very finely powdered, commercial, crystalline silicon, whose composition was first definitely ascertained by means of a complete qualitative and quantitative analysis, was used to reduce a large number of chemical compounds, which consisted chiefly of metallic oxides, chromates, tungstates, and molybdates.

2. Three methods for effecting the reduction were employed:

[63] Vigouroux, Compt rend. (1895), **120**, 367-70.

(1) The finely pulverized compound was mixed with the powdered silicon and heated in a test tube in a Bunsen flame. (2) The mixture was placed in a Hessian crucible and the reaction started by means of an ignition cherry, as in the Goldschmidt thermit process. (3) The reaction was induced by treating the mixture, in a Hessian crucible, with an electric arc formed between two electrodes of silicon. The latter substance was the same as that employed in the powdered form in the reaction mixture itself. Method 3, which is unique, and has hitherto not been employed, enabled one to start the reaction in many instances in which both Methods (1) and (2) failed. Furthermore, by means of Method (3) no additional foreign substances are introduced into the reaction mixture as is always necessarily the case when an ignition cherry is employed. Again, modifications of Method (3) may clearly be used as a means of starting reactions other than those studied in this research. In other words, the method is a new and general one which has proved very efficient. It is to be noted that in no case did the arc produce sufficient heat to support the reaction continuously, as would have been the case had the mixture been heated in an electric furnace. Indeed, the arc merely produced a high, very local kindling temperature. The reaction, once thus started, continued at the expense of the heat which it produced.

3. A series of ninety-two preliminary experiments was performed in which the three methods were employed. The results of these experiments have been presented in tabular form, and from them there were selected a considerable number of reactions that seemed especially promising for further study. The reactions thus selected were then studied in detail, the reaction products being isolated wherever possible, and the chief trend of the reaction represented by a chemical equation when the facts that could be established warranted it.

4. With the exception of Pb_2O (which did not react with silicon at all), the oxides of lead, namely, PbO, Pb_3O_4, Pb_2O_3, and PbO_2, were readily reduced by means of silicon, metallic lead and a slag of lead silicate being formed.

H. N. Warren's statement that a silicide of lead is formed when

silicon is heated with litharge could not be substantiated, for no silicide of lead was found.

5. The chromates, namely, $BaCrO_4$, $CaCrO_4$, $PbCrO_4$, and Na_2CrO_4, were all reduced by means of silicon, the silicide $CrSi_2$, and a slag of silicates of the respective metals being formed, except in the case of $PbCrO_4$ where no silicide was obtained. It will be recalled, from (4) above, that a silicide of lead does not exist.

The molybdates, namely, $BaMoO_4$ and $PbMoO_4$ yielded only slight reactions. Slags were formed, but neither free metals nor silicides were obtained.

The tungstates, namely, $BaWO_4$, $PbWO_4$, and Na_2WO_4, reacted with difficulty with crystalline silicon, yielding slags, but no free metals or silicides, except in the case of $BaWO_4$, where a few small globules, resembling silicides of tungsten in their resistance toward mineral acids, were formed.

6. The reduction of Cr_2O_3 by means of silicon was effected, a slag and the silicide Cr_2Si_3 being formed. This compound has never before been isolated, and so was not mentioned by either Watts or Hönigschmid, though Frilley claimed that such a silicide exists.

The oxides WO_3 and MoO_3 yielded only very local reactions when treated with silicon by Method 3.

Antimony oxide, Sb_2O_3, and bismuth oxide, Bi_2O_3, were reduced, forming slags and the respective metals.

Cobalt oxide, CoO, yielded metallic cobalt and a silicide whose exact composition could not be definitely established, because it was impossible to free the small particles of silicide completely from adhering slag.

Copper oxide, CuO, was reduced, a slag and a silicide, found to be Cu_4Si, being formed, but no metal was obtained.

Silver oxide, Ag_2O, yielded only oxygen and silver by Method 1. When Method 3 was employed, some SiO_2 was formed together with metallic silver. A light brown, poorly cohering substance was formed, which yielded oxygen on heating, indicating that it was an oxide of silver. Being intimately mixed with finely divided Si, SiO_2, and Ag, it was not feasible to isolate the oxide in question. H. N. Warren's claim that silver silicide is

formed when silver oxide and silicon react could not be substantiated. The general opinion that silicon dissolves in silver and crystallizes out from the latter on cooling is therefore probably correct.

Mercuric oxide, HgO, like silver oxide, yielded only the metal and oxygen by Method (1). By Method (3), a violent reaction took place, the products formed being mercury and silica.

Barium oxide, BaO, gave no reaction by Methods (1) and (2), and even by Method (3) the reaction was slight. A slag of barium silicate, but no silicide, was found.

Stannous oxide, SnO, was readily reduced even when heated with silicon over a Méker burner, metallic tin and silica being formed.

University of Wisconsin,
Madison, Wis.
February 18, 1921.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

THE APPARENT IRREVERSIBILITY OF THE CALOMEL ELECTRODE.[1]

By A. W. Laubengayer.[2]

Abstract.

Tests to determine whether the irreversibility of the calomel electrode is real or only apparent. The observed phenomena of irreversibility are explained as due to the formation of an adsorbed film of mercurous chloride on the mercury anode, which offers high resistance to the passage of the current. A current of 0.2 milli-ampere can pass before the film forms. A number of points about it are not yet cleared up, and call for further study.

[J. W. R.]

Paschen[3] has pointed out that a mercury anode polarizes much more strongly in hydrochloric acid than in sulphuric acid. He attributes this difference to the formation of a coherent film of calomel. Since there was no obvious theoretical reason why a mercury anode should behave differently in the two solutions and since the difference of behavior, if real, might have a distinct bearing on the behavior of the calomel electrode, Professor Bancroft suggested that I make some voltage-current runs under various conditions as part of my senior thesis. Preliminary qualitative experiments with a mercury anode in hydrochloric acid solution showed that the anode became coated with a black film having a high apparent resistance. In the quantitative runs, a piece of 7 mm. glass tubing was bent round at the bottom and blown so as to form a cup 2 cm. in diameter which was filled with mercury and served as the anode. The cathode was a small

[1] Manuscript received March 30, 1921.
[2] Senior Student, Cornell University.
[3] Wied. Ann. (1890), **39**, 61.

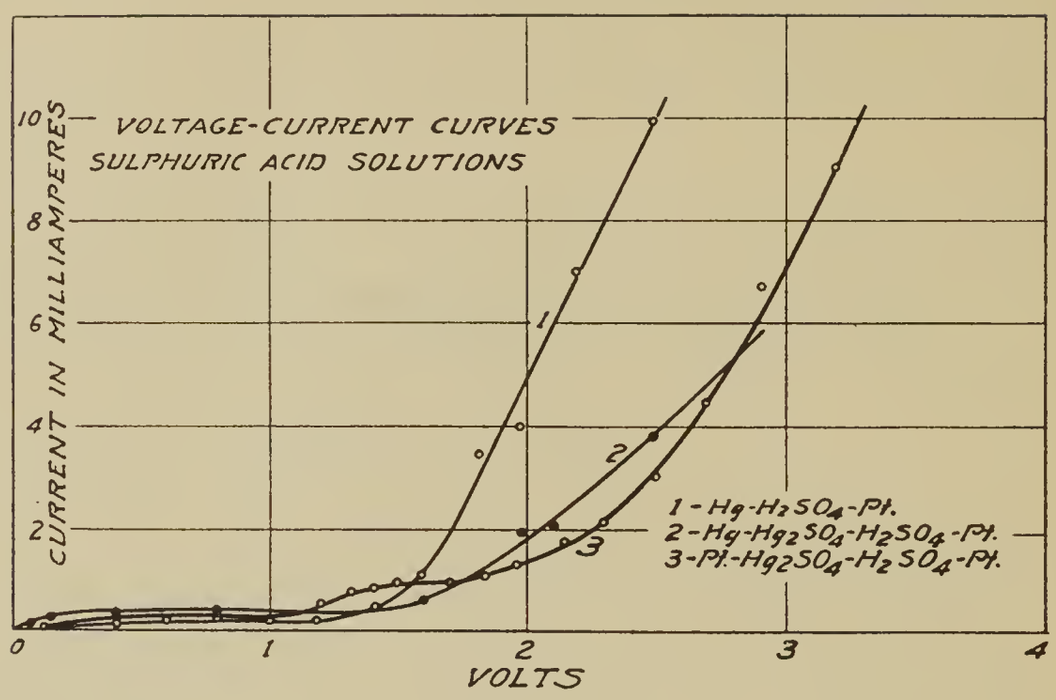


Fig. 1.

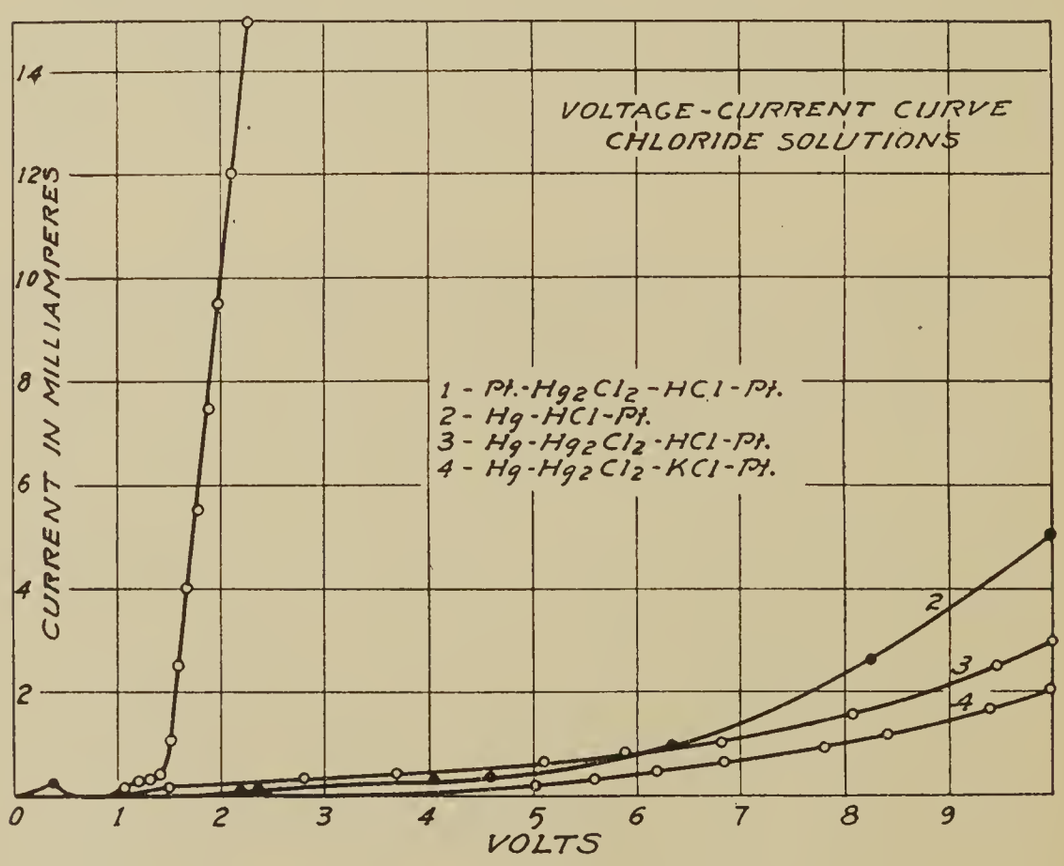


Fig. 2.

piece of platinum foil. In the runs with a platinum anode, the latter resembled the platinum cathode but was bent horizontally so that it could be covered with the mercury salt. The electrodes were placed in a glass beaker. A Leeds and Northrup student

potentiometer set was used to measure the voltage drop, while the current was measured with a very sensitive galvanometer for small values and on a milli-ammeter for higher values.

The following systems were studied:

Hg (anode) : *M/1* HCl : Pt (cathode).
Hg (anode) : Hg_2Cl_2 : *M/1* HCl : Pt (cathode).
Hg (anode) : Hg_2Cl_2 : *M/1* KCl : Pt (cathode).
Pt (anode) : Hg_2SO_4 : *M/2* H_2SO_4 : Pt (cathode).
Hg (anode) : *M/2* H_2SO_4 : Pt (cathode).
Hg (anode) : Hg_2SO_4 : *M/2* H_2SO_4 : Pt (cathode).
Pt (anode) : Hg_2Cl_2 : *M/1* HCl : Pt (cathode).

The mercury was the pure re-distilled product as obtained from the Department of Physics. The calomel was prepared by precipitation from dilute mercurous nitrate solution by pure hydrochloric acid. The mercurous sulphate was made by the electrolytic method as described by Clark.[4] Normal solutions of hydrochloric acid, sulphuric acid, and potassium chloride were made up in sufficient quantities so that all runs were made with the same solutions. The results for sulphuric acid are shown graphically in Fig. 1 and for the chlorides in Fig. 2, the voltage drop being measured along the abscissas and the current along the ordinates.

The curves in Fig. 1 are quite normal, the break coming at about the same place with the two mercury anodes and the curve rising less rapidly with the one for the solution containing mercurous sulphate, because of the increased resistance. Owing to lack of time no special study was made of the system with mercurous sulphate and platinum anode, as the important point for this investigation was merely the relative position of this curve as compared to the corresponding curve in the chloride solutions. In Fig. 2 we get a sharp break for the platinum anode; but the other three are quite abnormal. With a potential drop of six volts the current is less than one milli-ampere as against ten milli-amperes for two volts with a platinum anode, and as against four and ten milli-amperes with two and a half volts for a mercury anode in a sulphate solution. A high resistance film is evidently formed on the mercury in all the chlor-

[4] The Determination of Hydrogen Ions (1920), 157.

ide solutions. This is brought out more clearly in Fig. 3, which shows the behavior at lower voltages. The ordinates are galvanometer readings which can be converted into milli-amperes approximately by multiplying by 0.016.

With a mercury anode in hydrochloric acid and no mercurous chloride, a current of about 0.2 milli-ampere can pass before the film forms. When mercurous chloride is present in excess, the film forms at a lower current and lower voltage, but appears not to have quite so much resistance. There are a number of points

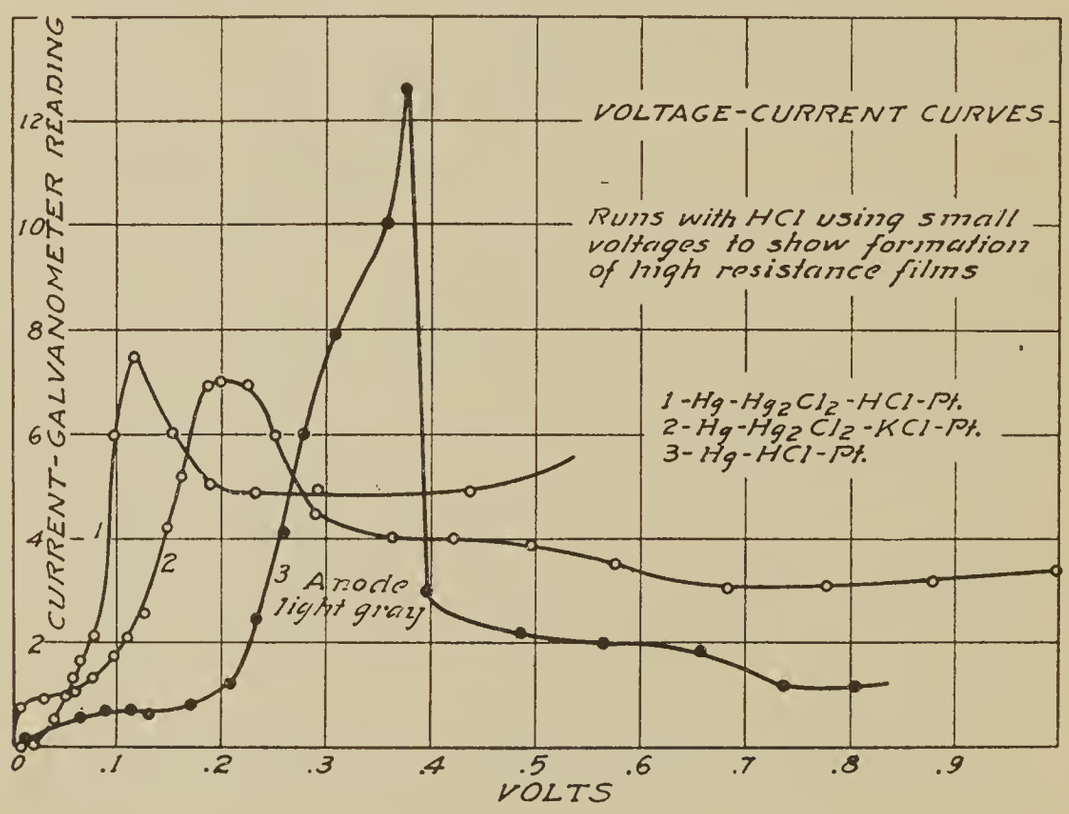


Fig. 3.

in connection with these experiments, which call for further study, but the only one that can be settled now is the composition of the high-resistance film.

With mercury as anode in hydrochloric acid a silvery-gray film formed at a low voltage, which became darker and finally quite black as the voltage was increased. The film was removed carefully and examined under the microscope. It appeared to be composed of finely-divided drops of mercury and some whitish, transparent, crystalline material. When this crystalline substance was treated with dilute ammonia it turned black, thus giving the test for calomel. Calomel was prepared electrolyti-

cally as recommended by Clark.[5] Under the microscope it presented practically the same appearance as the product obtained by anodic polarization.

The experiments show that the apparent irreversibility of the calomel electrode is not real, but is due to the formation on the surface of the mercury anode of a strongly adsorbed film of mercurous chloride, which offers a high resistance to the passage of the current. If this is scraped off as fast as formed, it becomes a simple matter to prepare calomel electrolytically[6] at a relatively low voltage. We do not know why mercurous chloride should behave so differently from mercurous sulphate in regard to forming a high-resistance film. I am indebted to Professor Chamot for aid in making the microscopic analysis and to Professor Briggs for suggestions in regard to many details of the work.

Cornell University.

[5] The Determination of Hydrogen Ions (1920), 135.
[6] Lipscomb and Hulett: Jour. Am. Chem. Soc. (1916), 38, 21.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

A PHOTO-ELECTRIC EFFECT IN AUDION BULBS OF THE OXIDE-COATED FILAMENT TYPE.[1]

By Theodore W. Case.[2]

Abstract.

Records the discovery of photo-electric effects from certain oxide-coated filaments of some high-vacuum Western Electric audion bulbs. Calcium, barium and strontium oxide cells were made, but the two latter principally worked with. The photo-electric current is proportional to the light intensity. The current for average sunlight is 100 to 150 micro-amperes. This is sufficient to run recording ammeters, and thus furnish a curve of daylight intensity. [J. W. R.]

It occurred to the author to investigate whether there might not be an emission of negative electrons from the oxide-coated platinum filaments of some high-vacuum Western Electric audion bulbs, due solely to the influence of light rather than heat. This was first tried by inserting a battery between the plate and filament, including a galvanometer, in series, the filament being made negative. A beam from a small arc light was concentrated on the filament, after passing it through a water-bath in order to eliminate the heat rays. This was first tried with the filament heated and it was at once evident, on the galvanometer, that a photo-emission was present. Next the filament, when cold, was exposed to the arc-light beam, and again a photo-electric effect was observed. The nickel plate was then made negative and a considerably greater photo-electric current was noted. Upon closely inspecting this plate a brownish deposit was observed. This deposit was determined as being the active material. It was

[1] Manuscript received March 7, 1921.

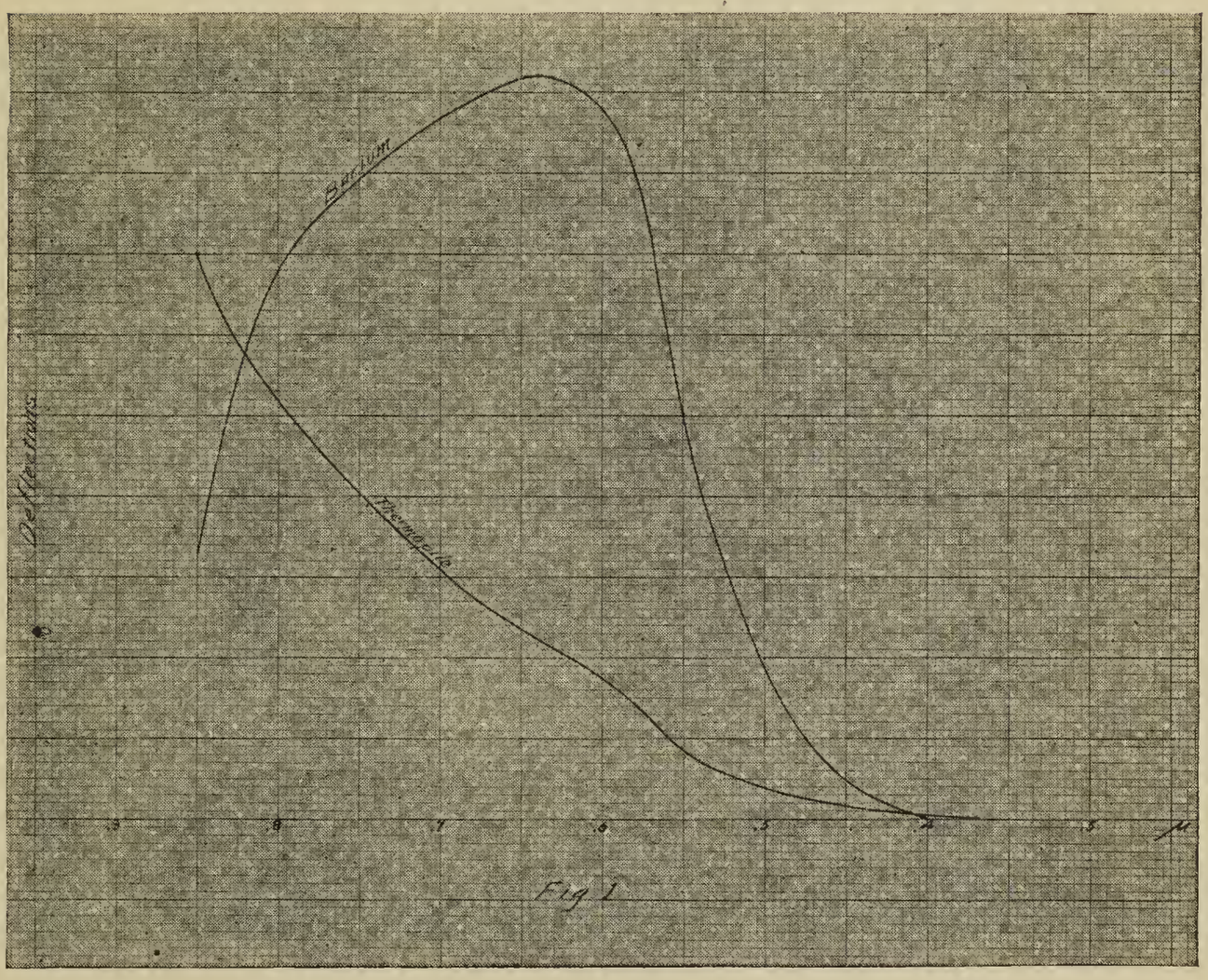
[2] Case Research Laboratory, Auburn, N. Y.

first thought that this might be a modified structural form of either barium or strontium oxide, or both. This bulb was broken open and then re-pumped and baked out, but no photo-electric action could be obtained after this treatment, indicating that the active deposit had been oxidized and that the deposit consisted of either barium or strontium metal, or both.

Experiments were then undertaken to find the correct condition for making separately either calcium, barium or strontium cells. It was finally determined that the necessary conditions for obtaining any of these three metals on a plate within an evacuated bulb opposite a platinum filament, on which was coated the oxide of the metal desired, were: first, an extremely high vacuum; second, the coated filament must be at the proper temperature, which differs materially for each of the above oxides; and third, there must be a certain electrical field intensity between the filament and plate, which may be alternating current and which is the same for any of the three oxides. If the field intensity be increased, no coating occurs. This is a fortunate circumstance, as it allows the heating of the nickel plate to a red heat, by electron bombardment, before coating so as to expel the occluded gases. The glass walls were baked in an electric oven and liquid air used on the mercury-vapor pump line. It was found that if the vacuum was not quite perfect at the beginning of the coating that it became so after the first few seconds, as the metals cleaned it up almost instantly.

In order to coat the barium, the filament temperature should be a bright orange; in the case of the strontium, it should be a white heat, as much as the platinum filament will stand for a short period. Only minute traces of calcium deposit have been obtained using a 20 percent iridium platinum filament burned as bright as it will stand for several minutes. It was found impossible to obtain even a trace of calcium when the filament was burned at the temperatures used for obtaining either barium or strontium. Therefore it was decided to use mixtures of either calcium and strontium oxide or calcium and barium oxide, as much better adherent coatings were obtained in this way. The method of coating the filament was to use mixtures of calcium and strontium nitrate and apply this to the filament heated in air so as to melt the nitrates and change them to oxides.

All of the work up to this time has been centered on barium and strontium cells. As they are now made, the nickel plate within the cell upon which is coated the deposit is 1⅜ inches by 5⅜ inches (3.5 x 13.5 cm.). The oxide-coated filament is used as the positive electrode in the completed cell. Up to this time all of the cells have been constructed with a high vacuum, rather than containing inert gases.



The barium cells show maximum action between the red and yellow when tested in the spectrum from a gas-filled tungsten light. (See Fig. 1.) The action falls off very sharply above the green. Below the red there is a sharp falling off, but, even so, there is quite a little action left in the infra-red beyond the visible. They have not been tested yet in the ultra-violet, as none have been made with quartz windows.

The strontium cells are more active to the shorter rays. The maximum action lies between the green and blue in the above

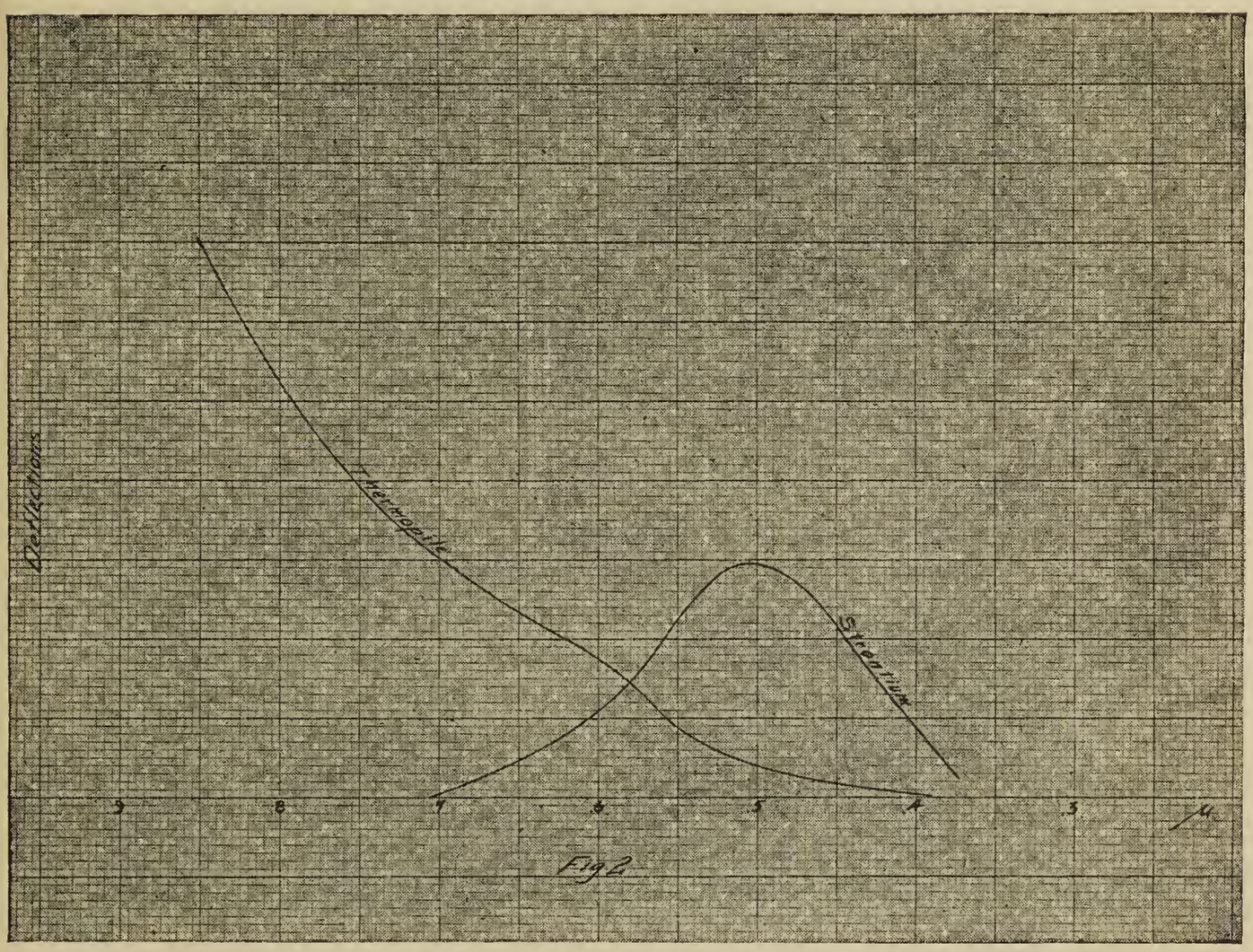
spectrum; there is no action in the infra-red or red. (See Fig. 2.) Indications are that they would be very active in the ultra-violet. There is no action of either cell to X-rays. The strontium cell is not affected by exposure to the strongest sunlight, but with the barium cell there occurs a very unusual reaction. Exposure to infra-red reduces the sensitivity of this cell and makes it insensitive to the shorter rays, blue and violet. If left exposed to sunlight for two or three hours the action is reduced 60 to 70 percent, and the spectral sensitivity curve is modified in the blue and violet, as above stated. If a water bath is placed in front of the cell for several hours, so as to eliminate the infra-red, the shorter rays will re-sensitize the cell to its former value. Exposure to a Cooper-Hewitt light will do the same thing. The cell will not recover if left in the dark after infra-red exposure. This reminds the author very much of the damping effect of infra-red radiation on certain phosphorescent substances under exposure to shorter rays, both of which may be due to the same reaction. As before stated, the strontium cell does not show this effect.

The photo-electric current from both of these cells is proportional to the light intensity to which they are active, from several foot-candles up to 4,000 foot-candles. They have not yet been tested beyond these limits. The current in average sunlight is approximately 100 to 150 micro-amperes.

The barium cells have a lower saturation voltage point than the strontium cells, 125 volts being sufficient for all barium cells although some were found to have a saturation point as low as 25 or 30 volts. One hundred and seventy volts is sufficient for all of the strontium cells. If the voltage be increased above the saturation point there is practically no increase in photo-electric current. If a voltage under the saturation point of a particular cell be used there becomes evident a creeping effect, and the photo-electric current does not reach its maximum immediately. This effect is such as is evident in selenium cells. However, if a saturation voltage be used the photo-electric current reaches its maximum immediately.

The barium cells show 3 to 4 percent change in photo-electric current for a range from —18° to +38° C., the strontium cells only half that. It was deemed advisable to make up a special small barium cell having for a plate a thin platinum foil so con-

nected electrically that a current could be passed through it in order to heat it to test for higher temperature effects. This was accordingly done and it was found that above 40° C. the photo-electric current increased very fast up to just below a visible red heat, after which the action fell off abruptly, which was probably due to gases from the foil which oxidized the barium, as the action did not re-appear after cooling. The maximum increase was



around one hundred times, and probably could have been much more at still higher temperatures if not spoiled by oxidation. Another interesting point was that there was very little current, due to thermo emission, when the light on the cell was turned off. This also suggests that the deposit is not an oxide.

The strontium cell has not yet been tested for higher temperature effects. When the photo-electric current of the barium cell is increased, due to high temperature, it was also noted that the action becomes sluggish just as though one of the effects of high

temperature had been to shift the saturation voltage point higher, but it could not be tested at the time whether a new saturation point could be reached, as there were no more batteries at hand.

The strontium cells have been tested for stability and durability and they are remarkably constant. They have been on test now for three or four months and as yet have shown no tendency to fall in action. They vary about two or three percent from day to day, but always along a mean line which has not fallen. They are exposed to the strongest sunlight without harmful effect. This should make them very useful for obtaining permanent records of daylight, as the current is amply sufficient to actuate an automatic recorder of the potentiometer type, such as the Leeds and Northrup machine used for recording temperatures with a thermo-couple. In fact, the author has been keeping permanent daylight records for several months now, and has already a very interesting set, together with barometer and temperature readings.

DISCUSSION.

B. S. Cushman[1]: This statement is correct except in one particular; the effect was first discovered from the oxide-coated filament, but the cells as they now stand show their activity from a deposit which is formed on the plate and which seems by all tests to be composed of metallic barium, or metallic strontium. The spectrum curves of the barium and strontium cells show that the barium cell has its maximum sensitivity between the yellow and the red, that curve is in the paper. The strontium cell shows its maximum sensitivity between the green and the blue. Exposure to any light, even the brightest sunlight, for apparently any period, makes no difference in the sensitivity of the strontium cell, but in the case of the barium cell we get a very marked effect.

J. W. Richards[2]: The action of a small amount of strontium in the barium suggests analogy with the Welsbach mantle phenomenon concerning thorium and cerium oxides; that is a pretty application of the same principle.

B. S. Cushman: That was the idea that led us to try the strontium and barium.

[1] Case Laboratory, Auburn, N. Y. Mr. Cushman presented the paper.
[2] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

ELECTROCHEMICAL ASPECTS OF PHOTOGRAPHIC DEVELOPMENT.[1]

By S. E. Sheppard.[2]

Abstract.

Discusses the previous work and adds information being developed at the research laboratory of the Eastman Kodak Company. Discusses the physical chemistry of the development reactions, and points out the present unsatisfactory value of the measurements by electrical methods, which are entirely relative to the particular experimental conditions. [J. W. R.]

The following paper is intended as a brief review of previous work along the lines of the title and an introduction to certain phases which are in progress in the research laboratory of the Eastman Kodak Company. The electrochemical aspects of photographic development can be rather easily grouped into two main divisions, the early, mainly historically interesting, attempts to represent the development process as an actual electrolytic silver deposition process, concretely assimilable to silver plating, and the later applications of the theory of solutions, particularly of the electrochemical theory, to the elucidation of the constitution of developing solutions and their characterization in terms of reduction potentials. Starting with the earlier, concrete electrolytic theories, we may note that analogy between photographic development and electroplating was first drawn by Lermontoff[3] specifically for so-called "physical" development. This consists in the use of an external silver nitrate solution, in conjunction

[1] Manuscript received March 19, 1921. Communication No. 121 from the Research Laboratory of the Eastman Kodak Company.

[2] Research Laboratory, Eastman Kodak Company, Rochester, N. Y.

[3] J. d. phys. Gesellschaft St. Petersburg (1877), IX, and J. M. Eder's Handbuch d. Phot. (1895), II, 45.

with an acidified reducing agent, *e. g.,* ferrous sulphate in aqueous sulphuric and acetic acid solution, pyrogallol in citric acid solution. Lermontoff asserted that "molecular galvanic elements are formed, out of the particles of ferrous sulphate, silver nitrate and metallic silver," the latter arising either from the action of exposure to light or due to development itself.

This type of explanation of development has not so much been contradicted or disproved as displaced. With the reasonable assumption that in such solutions a supersaturated solution of metallic silver is formed, which will deposit preferentially on metallic silver nuclei but actually may start depositing on various nuclei according to certain still largely unknown factors governing selective adhesion and adsorption to surfaces,[4] such explanations become superfluous.

The difficulties in eliminating differential action in preparing silver mirrors by chemical reduction processes offer illustrations familiar to most of us. Yet, as illustrating the vitality of this electrochemical conception we may note its appearance in R. Meldola's "Chemistry of Photography,"[5] while as marking its contact with and incipient transformation into the more modern doctrine we have to consider two papers given by H. E. Armstrong to the Camera Club, London, in 1892,[6] particularly the first entitled: "The Chemical Changes Attending Photographic Operation. I.—The Theory of Development in Relation to the Essentially Electrolytic Character of the Phenomena and the Nature of the Latent Image." This paper is historically very interesting. On the one hand there is re-stated, without apparent knowledge of Lermontoff's priority, the latter's forced analogy of development to the electrode position of silver, in this case to the De la Rue-Müller element,

$$Zn \mid ZnCl_2 \mid AgCl \mid Ag$$

while on the other hand there is a valuable application of the conception of balanced or reversible reactions to the process of development, which forms the basis of much in later theory. The close parallel to Lermontoff's thesis is evident on considering

[4] *Cf.* W. D. Bancroft: Applied Colloid Chemistry, 1921.
[5] R. Meldola, The Chemistry of Photography, 1891, p. 163.
[6] The Journal of the Camera Club, London (1892), 6, 61.

Armstrong's picture of physical development with "wet plates." For reduction of silver nitrate he proposes a reversible reaction, written

$$\underset{\text{Ferrous}}{2FeSO_4} + 2AgNO_3 \leftrightharpoons \underset{\text{Ferric salt}}{Fe_2(SO_4)_2(NO_2)_2} + 2Ag$$

He then states "There can be no doubt that in the liquid the interchanges thus pictured occur within voltaic circuits, and that as no action is observed where acid is present,[7] the algebraic sum of the currents in all these circuits is nil. It is to be supposed that on covering an exposed plate with such a solution the [latent] image acts like the silver rod [electrode] in the De la Rue-Müller cell, silver nitrate taking the place of the silver chloride, and ferrous sulphate that of the zinc rod [electrode] in the cell; hence the silver is necessarily deposited on the image." The picture is extended to alkaline development, or generally to so-called chemical development, of gelatin-silver halide, when the image is built up out of the solid silver halide particles. "When alkalies are used the image grows at the expense of the solid silver halide with which it is in contact, just as the silver wire in the De la Rue-Müller cell grows at the expense of the silver chloride cast around it."[8] In the case of hydroquinone the essential reaction is regarded by Armstrong as reversible and written:

$$\begin{array}{l} \text{Latent}|HgBr|HO|H \\ \text{Image}\ |AgBr\ |HO|H \end{array} \underset{\text{Quinol}}{C_6H_4O_2} \leftrightharpoons \begin{array}{l} \text{Latent}|Ag|BrH|OH| \\ \text{Image}\ |Ag|BrH|OH| \end{array} \underset{\text{Quinone}}{C_6H_4O_2}$$

Before development — After development

However, the presence of alkali is actually necessary and its function is regarded as that of neutralizing the hydrobromic acid formed in the above, giving instead the chain:

$$\begin{array}{l} \text{Latent}|AgBr|KOH|H \\ \text{Image}\ |AgBr|KOH|H \end{array} \underset{\text{Quinol}}{C_6H_4O_2} \leftrightharpoons \text{Image} \begin{array}{l} Ag|BrK|OH_2| \\ Ag|BrK|OH_2| \end{array} \underset{\text{Quinone}}{C_6H_4O_2}$$

the restraining influence of soluble bromides on development is debited to their being products of a reversible reaction.

[7] Free acid suspends the deposition of silver from this solution, organic acids have still more regulating action owing to formation of complexes.

[8] *l. c.* It should be noted that ferrous oxalate is a chemical developer in acid solution.

We must not delay further over this valuable yet in many respects dogmatically fallacious paper. It must suffice to point out that according to the naive electrolytic hypothesis the density, *i. e.,* the mass of silver, due to every exposure, however small, should tend to grow without limit other than the total mass of silver in the plate. The fundamental investigations of Hurter and Driffield[9] showed on the contrary that the density for each exposure tends to a limit fixed mainly by the illumination received; this has been amply confirmed by later investigations[10] and the conclusion drawn that each single silver halide grain develops as a unit, a prime function of the gelatin colloid being to secure this insulation and keep all development nuclei or germs from the silver halide grains other than those furnished by light.[11] But even supposing then that the "electrolytic process" as imagined by Armstrong takes place only for each exposed grain, there does not appear to exist sufficient true analogy to either a micro-electrolytic couple or to a cell to be of value. But taken as an abstract scheme rather than as a concrete picture, Armstrong's formulation of development contains much of value and outlines the essential elements for discussion of the measurement of the energy of developers, and the grading of developers in an electrochemical series. The next steps in this direction were consequent on the evolution of the theory of mass action, and the kinetic and thermodynamic theories of solutions. Following the installation of the ionic theory by Arrhenius, the first working definition of reduction and oxidation potentials was given by W. Ostwald.[12] As an electrochemical measure of the intensity factor of chemical energy in reduction-oxidation reactions, he proposed determination of the potential differences at unattackable electrodes immersed in the two solutions, these latter being connected by a liquid: liquid contact, the electrodes metallically, *i. e.,* in an electromotive combination. Measurements for a number of oxidizing and reducing

[9] F. Hurter and V. C. Driffield, J. Soc. Chem. Ind. (1890), **10**, 455.

[10] S. E. Sheppard and C. E. K. Mees, "Theory of the Photographic Process," p. 52 (Longman, 1907).

[11] *Ibid.*

[12] Chemische Fernwirkungen Z. phys. Chem. (1892), **9**, 540. In this paper a number of examples are given of similar actions to that cited by Lermontoff in support of his theory.

solutions were made in this way by W. D. Bancroft.[13] These values were used by G. Bredig[14] to set up a scale of reduction potentials of developers, reproduced here.

Solution	Single Potential Volts
$Sn\ Cl_2$ in KOH aq.	+0.30
$NH_2\ OH$ in KOH aq.	+0.06
Pyrogallol in KOH aq.	—0.08
Hydroquinone in KOH aq.	—0.23
Hydrogen in HCl aq.	—0 25
Potassium ferrous oxalate	—0.29
Ag Br in 0.1 n KBr	—0.42
Ag Cl in 0.1 n KCl	—0.57
Na_2SO_3	—0.58
$Na_2S_2O_3$	—0.58
Potassium ferrocyanide	—0.60
Hydroxylamine in acid	—0.64
Sodium bisulphite	—0.66
Ag Br in H_2O	—0.73
$FeSO_4$ in acid	—0.79
Ag Cl in H_2O	—0 80
Potassium ferric oxalate	—0.85
Iodine in potassium iodide	—0.89
Nitric acid	—1.26
Bromine in potassium bromide	—1.43

The silver halide potentials were taken from measurements by Zengelis[15] and Goodwin.[16] This scale, however, could only be regarded as rough approximation or tentative ordering. For, as pointed out by M. Le Blanc,[17] these determinations were deficient in this respect, that no definite concentration of reaction-products were present, but so-called "pure" reagents. Just as for an electrode of a metal immersed in a solution of its salt, there holds also for oxidation-reduction cells the van't Hoff equation[18] for the reaction isotherm in the form

$$\pi_0 = \frac{RT}{nF} \log k$$

[13] Uber Oxydations Ketten, Zeitschr. f. phys. Chem. (1892), **10**, 387.
[14] J. M. Eder's Jahrb. f. Phot., 1895, p. 19.
[15] Zeitschr. f. phys. Chem., **12**, 305.
[16] *Ibid.*, **13**, 645.
[17] Lehrb. d. Elektrochem. 1ste Auflage, p. 191.
[18] R. Peters, Uber Oxydations und Reduktionsketten Zeit. Phys. Chem. (1898), **26**, 193.

where n is the change of valency, F the Faraday constant, k the equilibrium constant of the reaction. For any other than equilibrium conditions we have[19]

$$\pi = \pi_0 - \frac{RT}{nF} \log \frac{C_1^{p_1} C_2^{p_2}}{C_1^{q_1} C_2^{q_2}}$$

for example, with a ferrous-ferric salt solution this reduces to

$$\pi = \pi_0 - \frac{RT}{nF} \log \frac{(Fe^{++})}{(Fe^{+++})} \quad .$$

and when (Fe^{++}), the concentration of ferrous ions, equals (Fe^{+++}), the concentration of ferric ions, $\pi = \pi_0$.

Peters showed that for a number of inorganic combinations the above relation held satisfactorily.

Following Ostwald's application of the ionic theory to oxidation and reduction, by the former is to be understood a process of increase of positive charges, or diminution of negative charges, by reduction one of increase of negative charges, diminution of positive ones. In considering how a p. d. between electrode and electrolyte could arise between a noble metal, *e. g.,* Pt, immersed in a reduction-oxidation mixture, *e. g.,* of ferrous and ferric salt, Le Blanc,[20] Luther[21] and others inclined to consider it due to direct exchange of charges between electrolyte and electrode. On the other hand, Nernst[22] brought in here the older conception of oxidation and reduction as related to oxygen addition (or hydrogen subtraction) and hydrogen addition (or oxygen subtraction) in the following form[23]: "Since an oxidizer can be considered as a substance which in aqueous solution can evolve oxygen, either *per se* or by decomposition of water, while a reducer can afford hydrogen in an analogous way, it is thermodynamically permissible to refer the e.m.f. of oxidation-reduction cells to the e.m.f. of a

[19] If the Nernst formulation that the current flows from metal to solution when metal is positive is used, the sign in the equation should be negative. *cf.* F. Haber Zeit. Elektrochem. F. (1901), 1047. Peters measured the e.m.f. of a normal calomel cell one side and a ferrous-ferric mixture Pt, on the other. In his paper he followed Le Blanc's recommendation of setting the potential of the metal equal to zero, the p. d. Hg : HgCl in normal KCl therefore as —0.56, and gave the positive sign.

[20] *loc. cit.*

[21] Zeitschr. phys. Chem. (1901), 36, 357.

[22] Theoret. Chem. 3d Edit. p. 673, Zeitschr. f. Elektrochem. (1910), 16, 519.

[23] *loc. cit.* Zeitschr. f. Elektrochem., p. 517.

hydrogen : oxygen (gas) cell." The conception that the potentials of oxidizers and reducers are to be referred to oxygen or hydrogen gas charging of the electrodes has the advantage of rigid concatenation with Faraday's law, that the passage of electricity between electrode and solution only takes place through material ions. The equivalence of the two conceptions was discussed theoretically and experimentally by Fredenhagen[24] working under Nernst's direction. Looking at the matter from the reduction-potential side, Nernst's view means that a Pt or Pd electrode in a reducing solution behaves as if charged with hydrogen according to the equilibrium

$$\frac{(\text{Reducer}) \times (H^+)}{(\text{Oxidizer}) \times (H)} = K \quad (25)$$

the terms in the brackets referring to concentrations[26] of the electromotively active components. Consequently, substituting into Peters' equation, we have

$$\pi = \pi_0 - \frac{RT}{nF} \log \frac{(H)}{(H^+)}$$

Since atomic H concentration is defined by the equilibrium

$$\frac{(H)^2}{(H_2)} = K_H \; i.e. \; (H) = K_H^{1/2} H_2^{1/2}$$

we can write

$$\pi = \pi_0 - \frac{RT}{nF} \log K' \frac{(H_2)^{1/2}}{(H^+)}$$

or

$$\pi = \pi'_0 - \frac{RT}{nF} \log \frac{(H_2)^{1/2}}{(H^+)}$$

[24] C. Fredenhagen, Zur Theorie der Oxydations-und Reduktionsketten, Zeitsch, anorg. Chem. (1902), 29, 396.

[25] *cf.* W. M. Clark, "The Determination of Hydrogen Ions," 1920, p. 175, *et seq.* (Baltimore, Williams & Wilkins Company).

In Fredenhagen's terminology

$$\frac{RT}{(m-n)F} \log \frac{P_1 C(Me^{n+})}{C(Me^{m+})} = \frac{RT}{F} \log \frac{PH_2}{pH^+}$$

where P_1 is Le Blanc's "transformation constant" for the Me^{n+} ions, *cf.* Fredenhagen, *loc. cit.*, p. 421.

[26] The limits of the Nernst equation, and the problem of the relation of concentration, active masses, osmotic pressures and "activities" are not considered here, the gas laws being supposed to hold.

which is identical in form with the general equation for the hydrogen electrode

$$\pi = \pi_0 - \frac{RT}{F} \log \frac{(H_2)^{1/2}}{(H^+)}$$

Here by definition $\pi_0 = 0$, for the p.d. at the normal hydrogen electrode. Hence, if potential differences are referred to on this basis $\pi_0 = \pi'_0$, and the π of any oxidation-reduction equilibrium may be expressed in terms of the π of a hydrogen electrode.

Without at this point criticizing the validity of the minute hydrogen pressures this would often involve[27] we may note that in itself the assumption of "equilibrium between hydrogen and hydrogen ions in harmony with the equilibrium between oxidation and reduction products in a solution, and that wherever we have such products present the electrodes are charged with hydrogen at some definite pressure"[28] raises an important issue for the subject under review. This is the validity of the best electrochemical determinations yet made of the reduction potentials of photographic developers by their single potentials, *viz.,* those due to F. C. Frary and A. H. Nietz.[29] Their work was based on the following premise. "In order to determine the absolute pressure of hydrogen represented by a given single potential π_x of a developer it is only necessary to also determine, in the same solution, the potential πH_2 of a platinized electrode saturated with hydrogen at atmospheric pressure. For two hydrogen electrodes in the same solution, but saturated with hydrogen at different pressures, the difference of potential is represented by the formula

$$\pi = 0.0001983\ T \log \frac{p}{p'}$$

Where p and p′ represent the hydrogen pressures. Since in one case the pressure is one atmosphere p = 1 at 25° C., and the equation becomes

$$\pi = 0.05909 \log \frac{1}{p'}$$

[27] *cf.* Clark, *loc. cit.*
R. Luther, Zeitschr. f. Elektrochem. (1910), 16, 519.

[28] W. M. Clark, *l. c.,* p. 178.

[29] The Reducing Power of Photographic Developers as Measured by Their Single Potentials, J. Amer. Chem. Soc., 37, 2246.

this being the difference between the hydrogen potential of the developer and its single potential, *i. e.*, $\pi = \pi H_2 - \pi_x$. The partial pressure of hydrogen, p′, seems to be the only absolute standard to which the reducing power of the developer can be referred."[29] Although Frary and Nietz obtained[30] satisfactorily constant potentials for certain solutions—amidol in one week, hydroquinone in over three months—these being carefully freed from oxygen, it is doubtful if these values can be regarded in any way as absolute. For if they represent absolute equilibrium states, and not merely stationary states, then they must represent true equilibria between the $\frac{(H)}{(H^+)}$ value and the $\frac{[\text{reduction product}]}{[\text{oxidation product}]}$ as demanded by the Nernst-Fredenhagen harmonization of the two theses as to oxidation: reduction potentials. Now, on the contrary, we have little evidence for, and much evidence against, the attainment of true equilibrium between reduction products and oxidation products in alkaline solutions of organic developers. Indeed, no variation of this ratio is attempted by Frary and Nietz, so that their potentials are subject to the criticism made by Le Blanc and Peters with respect to Bancroft's early measurements.

As already stated, the reversibility of development had been asserted by Armstrong, but without experimental evidence. As this paper is concerned primarily with the electrochemical aspects of development the contingent chemical investigations will not be analyzed here. It may be noted, however, that the reversibility of development of gelatino-silver halide plates by ferrous oxalate indicated by Friedlander[31] was quantitatively confirmed by the writer,[32] but the reversibility with alkaline solutions of organic developers has been shown to be actually greatly interfered with by secondary reactions between the primary oxidation products and the alkali and sulphite of the developing solutions.[33] A semi-empirical method for determining the reductions potentials of such

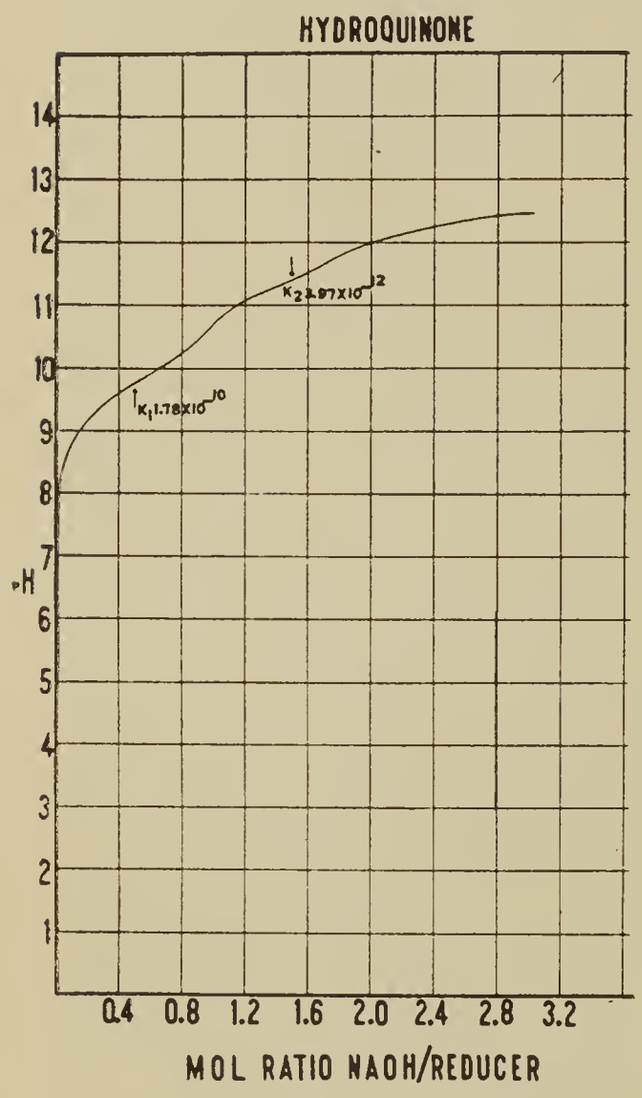
[30] *l. c.*, p. 2261.

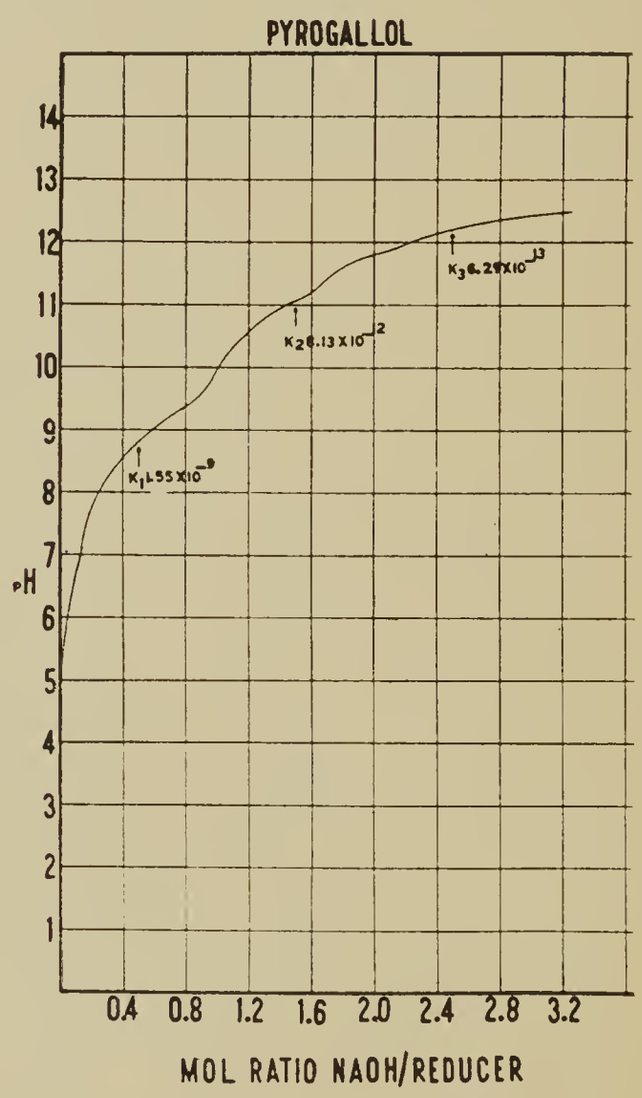
[31] Photog. Correspond. (1902), p. 252.

[32] Theory of the Photographic Process (1917), p. 92.

[33] S. E. Sheppard and C. E. K. Mees, "Theory of the Photographic Process, p. 151, *et seq.* R. Luther and A. Luebner. The Chemistry of Hydroquinone Development, Brit. Journ. of Phot., 1912, p. 632. N. Schilow and S. Fedotoff. Physikalisch-Chemische Studien an Photographischen Entwicklern. Zeit. f. Elektrochem. (1912), 18, 929. M. A. Gordon, the Silver Equivalent of Hydroquinone, Journ. Phys. Chem., 9

developers, depending upon determining the soluble bromide concentration producing equal depressions of density, was worked out by the writer[34] and has recently been improved and extended by A. Nietz.[35] The values thus obtained are, however, largely empirical, and are further uncorrected for the stoichiometric reducing power, *i. e.*, atoms silver ultimately reduced per equivalent of





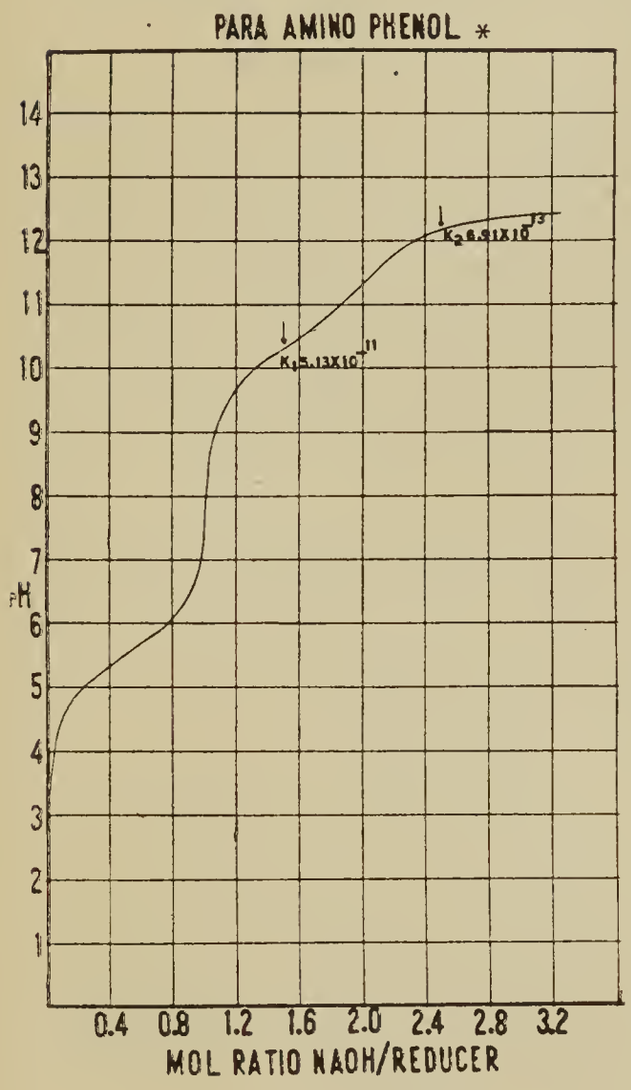
reducer. This latter determines the value n in the free energy and reduction potential equations. Various investigators[36] have found considerable differences, for one and the same reducer, in this quantity, according to their experimental conditions. Hence, it appears that before satisfactory absolute reduction potentials for organic reducing reagents can be determined, the ground requires to be cleared in the following directions:

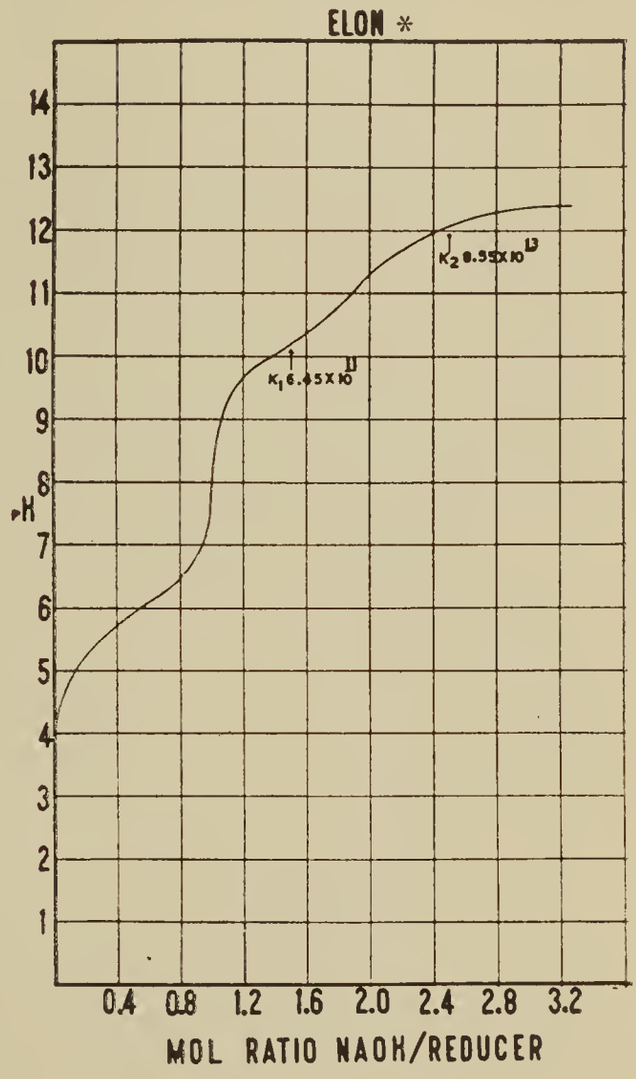
[34] *cf.* Theory of the Photographic Process, p. 188.
[35] A. H. Nietz. The Photographic Journal (1920), **60**, 280.
[36] *cf.* M. A. Gordon, Journal Physical Chemistry, *loc. cit.*

a. Determination of the state in solution of the reducing agents.

b. Nature, and to some extent, kinetics of the reaction in development.

c. Silver equivalent of the reducer in the working period of development.





From this a more definite estimate of the probable value of reduction-potential measurements will be possible. At present, the measurements by electrical methods are entirely relative to the particular experimental conditions, and to a large extent, accidental. Their technical value is very uncertain, being very much less in this respect than the bromide depression method of Sheppard and Nietz, which gives directly the photographically desirable characteristics. The inutility photographically of the electrochemical measurements is likely to be the greater, the longer the

*The hydrochlorides of these substances were taken, and the lower parts of the curves (first neutralization period) show the neutralization of the hydrochloric acid.

time taken to reach "equilibrium"—or at any rate, constant potentials, owing to the secondary reactions referred to. There appears a possibility of more satisfactory results, both theoretically and practically being reached by application of alternating current electrolysis methods[37] to the system

Ag|AgBr : KBr aq Developer|Neutral salt bridge| Developer : KBr aq : AgBr|Ag

and this is being investigated. Meanwhile, in regard to problem (a) determination of the state in solution of the reducing agents, some progress has been made in the investigation of their acidic function. With F. A. Elliott and Alice D. Duschak titration curves, using a hydrogen electrode, were determined for p-aminophenol, hydroquinone, pyrogallol, and elon (methyl p-aminophenol) shown in the diagrams. The ionization constants computed from these are as follows:

Developer	K_1	K_2	K_3 at 25° C.
p-amino phenol.....	5.13×10^{-11}	(6.91×10^{-13})	.....
Elon	6.45×10^{-11}	(8.55×10^{-13})	.....
Hydroquinone[38]	1.75×10^{-10}	(3.97×10^{-12})	.....
Pyrogallol	1.55×10^{-9}	(8.13×10^{-12})	(6.29×10^{-13})

The values enclosed in brackets are not definitely indicated by marked changes in curvature of the neutralization curve, and hence must be regarded as to some extent hypothetical. This lack of definite change of curvature is, however, to be expected when the two ionization constants lie so close together.[39]

[37] *cf.* D. Reichinstein Zeitschr. f. Elektrochem. (1909), **15**, 734, and *ibid.* (1910), **16**, 916.

[38] H. Euler and Il Bolin. Uber die Dissociationsconstanten der Dioxybenzole, Zeitschr. Phys. Chem. (1909), **47**, 71, found 1.1×10^{-10} for K_1.

[39] For previous work on the second dissociation constants, see Thiel and H. Römer, Zeitschr. physik. Chem. (1908), **63**, 711, and criticism by G. Bruni, Zeitschr. für Elektrochem. (1908), **14**, 701, 709.

Rochester, N. Y.
March 9, 1921.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

THE ELECTROLYTIC MANUFACTURE OF PARAMINOPHENOL.[1]

By A. S. McDaniel, L. Schneider and A. Ballard.[2]

Abstract.

Paraminophenol sulphate was made by electrolyzing nitrobenzene in solution in strong sulphuric acid as a catholyte, using platinum electrodes, with a cathode current density of 3-4 A. per sq. dm., and anode density double. Ice cooling was necessary for best yields. Diaphragms were used of thin dense unglazed porcelain. Sulphuric acid was used as anolyte. All the nitrobenzene was reduced at an ampere efficiency of approximately 50 percent; the other products were mainly sulphonic acid and aniline. The product was centrifuged and treated with HCl, giving paraminophenol hydrochloride of high purity. [J. W. R.]

Shortly after the beginning of the war when all chemical supplies were cut off from Germany the shortage of photographic developers became very acute. The prices jumped to abnormal figures with the supply on hand steadily decreasing.

Experimental work was at once started by the Eastman Kodak Company to increase the number of the developers which they were manufacturing, and since paraminophenol is used both directly and as an intermediate in the preparation of other developing agents, work on various methods of production was started. At this time there were literally no intermediates obtainable, the usual compounds used for the synthesis of paraminophenol—phenol, chlorbenzene, and aniline—were all unavailable on the market, and among the methods tried the process of electrolytic reduction offered the advantage that it utilized as the starting

[1] Manuscript received March 19, 1921. Communication No. 69 from the Research Laboratory of the Eastman Kodak Company.

[2] Research Laboratory, Eastman Kodak Company, Rochester, N. Y.

point nitrobenzene, which could be made very easily and with a very simple plant. It was decided, therefore, to attempt production by the electrolytic reduction of nitrobenzene in sulphuric acid, first in the laboratory and then on a small manufacturing scale purely as an emergency measure but with a view also of determining what possibilities, if any, the method offered for development into a practicable process under normal conditions.

The present paper is a brief and somewhat cursory account of the results obtained and the methods employed in this work.

As is well known, nitrobenzene in acid solution is reduced to phenyl hydroxylamine, and under favorable circumstances this undergoes molecular rearrangement into paraminophenol.[3]

The nitrobenzene may be reduced either in solution in strong sulphuric acid or in suspension in more dilute acid. The former procedure was adopted as best suited for quick development under the conditions obtaining at the time, and as being most likely to give a regular output in continuous operation. Most of the methods described in the literature in which concentrated acid was used were found on trial to yield almost entirely the sulphonated derivative of paraminophenol. This product is practically useless as a developer or as an intermediate for the production of a developer. It was soon determined that sulphonation is due to the use of sulphuric acid of too high concentration or to too high a temperature, or to both these factors combined.

On the other hand, if the concentration of acid is too low the nitrobenzene separates from solution resulting in very poor current efficiencies and in a low percentage reduction of the nitrobenzene. This difficulty is further increased by the unavoidable dilution of the acid which results from the reducing action at the cathode, also if dilute acid is used in the anode compartment this will cause a further dilution of the acid in the cathode compartment by diffusion through the diaphragm. For these reasons the allowable range of concentration of acid was found to be quite narrow at least for any practically useful current densities. The best range of concentration was found to be from about 90 to 91 percent of H_2SO_4 by weight.

In the earlier experiments almost the whole product consisted

[3] Elbs, "Electrolytic Preparations," and Loeb, "Electrolyses and Electro-syntheses of Organic Compounds."

of the sulphonic acid; but after several laboratory runs, the yield of paraminophenol was considered high enough to continue work on a small commercial scale.

The preliminary laboratory experiments showed that platinum was the best material for both electrodes, that the electrolyte must be kept free from contamination with iron or other heavy metals, that water or ice-cooling was necessary for the best yields of paraminophenol sulphate with minimum sulphonate, and that the best cathode C. D. is 3-4 amp. per 100 sq. cm. with the anode density approximately double that of the cathode. Smaller anodes were found to be impracticable because of excessive spraying due to the too rapid evolution of oxygen gas. All attempts to produce paraminophenol without using a porous diaphragm failed; a thin but very dense porous porcelain diaphragm gave the best results.

A sufficient quantity of platinum for electrodes was obtained and experiments were then carried out on a semi-commercial scale.

Electrodes: Separate electrodes with external metallic connections were used. Intermediate or bi-polar electrodes were not employed since it was decided that frequent removal for cleansing and examination would probably be necessary in a small scale experimental plant until the most favorable conditions for continuous operation on a larger scale could be determined.

Cathode: A sheet of platinum 25.4 cm. wide and 30 cm. long (approximately 1,000 sq. cm.) and 0.075 mm. thick, gave good results. Gold or platinum-plated gold, gave results that compared favorably with those obtained from platinum electrodes. Graphite did not give good results, due to iron. Carbon gave better results than graphite.

Anode: Platinum was found to be the only substance that gave good yields, lead anodes giving too much sulphonic acid mixed with the sulphate, and favoring the formation of aniline.

Electrode Mountings: The fumes rising from the cells during electrolysis were found to be very corrosive, resulting in a contamination of electrolyte with copper and iron salts derived from this corrosive action of the fumes upon the metal leads. A good

deal of trouble was experiencend in designing a mounting that could be placed directly over the cell, making a good connection to the electrode that would not be readily corroded by the fumes. Two-piece wooden mountings thoroughly impregnated in melted paraffin wax were finally used, for protecting the metallic leads from the fumes. The sheet platinum electrodes were clamped to the copper wire leads by means of these two-piece wooden mountings or coverings which served to hold the leads in position and also to protect them from the action of the fumes and spray. This arrangement was quite effective in preventing contamination of the electrolyte.

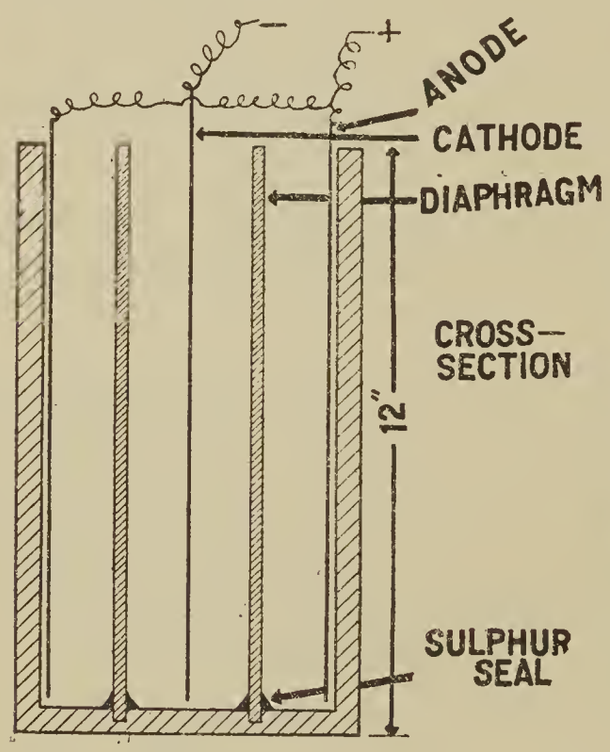


Fig. 1.

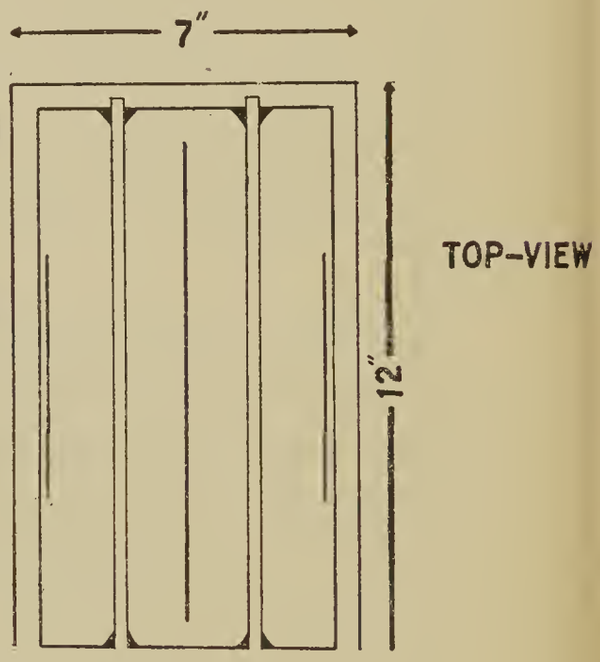


Fig. 2.

Cells: The first cells used were made of Alberene stone but these did not give good results, for after being in service for some time the stone was attacked by the nitrobenzene-sulphuric acid mixture resulting in the stone swelling and flaking off into the product and causing the cells to leak. Glazed earthenware cells were then obtained and these gave good results. The general construction of the cells and arrangement of the electrodes is illustrated in the accompanying diagram, Figures 1 and 2.

Diaphragms: Various types of diaphragms were tried and finally diaphragms specially made by the Locks Insulator Company and later by the Coors Company were found to be satisfactory.

The diaphragms were 12 x 12 x ¼ inches (30 x 30 x 0.6 cm.) and were made to adhere to the cells by pouring melted sulphur through a clay mould connecting the diaphragm to the cell and allowing it to cool. It was found that the sulphur did not adhere firmly to the glazed porcelain of the cell but upon first removing the glaze and then pouring, the sulphur held the diaphragm firmly in place and gave excellent service.

Sulphuric Acid: It was found necessary to use acid free from iron or heavy metals. Commercial acid was tried but the iron produced poisoning effects resulting in the production of aniline. The use of arsenic-free acid was not, however, found necessary.

Nitrobenzene: To the crude commercial product, sodium carbonate was added to neutralize it and this was distilled in an iron still.

Hydrochloric Acid: Both C. P. and commercial quality acid were used, the C. P. acid being used for the final precipitation and the commercial acid for the preliminary washing of the cell sludge.

Preparation of Aminophenol Sulphate

Forty cells were arranged in banks of ten, each bank being controlled by a separate control switch and each cell controlled by an individual switch. Provision was made to add resistance to any bank of cells to control the current. The cells were set in a tank of water cooled by brine coils to control the temperature.

Into the cathode compartment a mixture of 540 cc. nitrobenzene and 1,800 cc. of 91 percent sulphuric acid was introduced, while both of the anode compartments were brought to the level of the catholyte with sulphuric acid of sp. gr. 1.75. The electrodes were then placed in the electrolytes and connected to the source of current and 60 amperes passed through the cell for 24 hours which is approximately twice as much as necessary to reduce the 650 grams of nitrobenzene according to the equation:

$$C_6H_5NO_2 + 4H = C_6H_4.OH.NH_2 + H_2O.$$

The voltage was approximately 8 volts per cell, of which about 4 volts was due to the voltage drop through the diaphragm.

The temperature of the cells was kept at 30° C., higher temperatures giving an increasing amount of sulphonate. Twice a day

water was added to the anolyte to replace loss by evaporation and to keep the sp. gr. approximately the same as at the start of the run. On completion of the electrolysis the catholyte was syphoned from the cell into stoneware crocks which were placed in a cooling tank and kept at 0° C. for 12 hours. During this time a considerable quantity of paraminophenol sulphate separated from the mass.

Purification: The contents of the crocks from the cooling tanks was poured on a porous porcelain filter in a large filter device and suction applied until almost all of the sulphuric acid was drained from the sludge of sulphate and sulphonate. It was impossible to dry this sludge completely, as the sulphuric acid took up moisture too rapidly.

The partially dried sludge was then placed in stoneware crocks and covered with concentrated commercial hydrochloric acid. This mass was thoroughly stirred to remove free sulphuric acid and then centrifuged through a felt bag on a rubber-covered basket centrifuge. The filter bag was removed and the contents emptied on glass trays which were dried in an air oven at 40° C. over night. The crude dry product obtained was transferred in 20 pound (9 kg.) lots to a stoneware tank and made up to a mush with hot water; live steam was then passed into the mass through a rubber hose until it just reached the boiling point. Just enough water was added to dissolve the mass. (Complete solution is not effected, as the mass always contains a varying amount of sulphonate which is very insoluble). 3.5 pounds (1.6 kg) of filchar or bone charcoal and 2.5 pounds (1.1 kg.) of sodium bisulphite were added and the mass brought just to the boiling point with constant stirring and kept at this temperature for about 20 minutes, when it was filtered through 2 layers of closely woven canvas, on a suction filter. The filtrate from this filtration was colored from a light amber to a dark wine color and if too dark it was returned to the crock and again purified as above. The color of this filtrate determines the color of the final product, so this should be as nearly water white as possible. It was then run into a stoneware crock, an amount of C. P. hydrochloric acid approximately equivalent to the volume of the filtrate was added, and the crystals allowed to separate out overnight at 0° C. These

crystals were centrifuged through felt bags and dried in an air oven at 40° C. over night.

The product from this purification is of a light gray or gray-white color with no odor of free hydrochloric acid. A yield of about 40 to 50 percent of the theoretical amount of paraminophenol is directly obtained. An additional 10 percent (approximately) remains in the sulphuric and hydrochloric acid mother liquors which were not regularly worked over for recovery of paraminophenol. Practically the whole of the nitrobenzene was reduced The remaining reduction products consisted mainly of the sulphonic acid and aniline.

In another method of purification tried, the partially dried cell sludge was spread out on porous porcelain plates which soaked up the excess sulphuric acid. The product from this drying is a white powder which is dissolved in water and heated with sodium bisulphite and filchar, filtered, and hydrochloric acid added to the filtrate to precipitate the hydrochloride. This gave a very white product, but the method of drying the sludge is very slow and after the porous plates have been used once they have to be dried out by heat.

Output: From a plant of 40 cells as described and operated by four men the yield of finished product averaged 125 to 150 pounds (57 to 69 kg.) per week. The amount of finished product averaged 8 to 10 ounces (226 to 280 g.) per cell per 24 hours run.

Remarks

Shortly after the start the catholyte turns blue or blue-gray, the color increasing during the run. The color of the product formed is not constant, as it varies at the end of each run from a gray crystalline mass to a dark blue viscous liquid. The gray crystalline mass is more desirable.

It was invariably found that if the color turned brown or black during the electrolysis the yields obtained were very small. Also, once a cell was poisoned it had to be thoroughly cleaned before starting a new run, or the same condition recurred.

These cells were cleaned by washing with water and were then allowed to soak in water for several days to ensure that the diaphragms were clean. When again placed in the bank and

allowed to run good yields were obtained. The introduction of small amounts of iron or copper into the cells caused a poisoning effect as described. There is some slight loss of platinum at the anode, due to corrosion. This was kept at the lowest figure by keeping the anolyte from becoming too concentrated, as concentrated acid gives the highest loss.

At times during the electrolysis the catholyte would foam up over the top of the cells; this was remedied by using an excess of nitrobenzene which formed a layer which floated on top of the nitrobenezene-sulphuric acid mixture. Burning off the electrodes after each electrolysis seems to increase the yield. A draught hood must be erected over the cells, as the fumes that arise during the electrolysis are very irritating.

The approximate yields are tabulated below:

Current yield	=	25 percent approximately
Chemical yield on nitro benzene	=	40-50 percent approximately (exclusive of mother liquors)
Yield per kilowatt hour	=	40-50 g.
Yield per man hour (emergency equipment)	=	7-8 oz. (200-226 g.) approximately

Conclusion

With all-platinum electrodes and also with platinum plates, gold cathodes and platinum anodes, the process gave a regular output of paraminophenol hydrochloride of a high degree of purity and good quality for use as a developer.

The relatively high cost of production was not due in the main to the use of platinum, since the value of the investment in platinum relatively to that of the product would not be excessive in comparison with similar electrochemical processes, and the charges for interest and loss of platinum were not serious items in the cost.

Aside from labor, by far the largest single item in the operating cost was the sulphuric acid and any process based on this method to be commercially successful under normal conditions must provide for the cheap concentration of the spent acid. This must be done without contaminating the acid with iron, lead, or other heavy metals.

In addition to the cost of the acid much hand labor was required and the upkeep was considerable owing to the corrosive

action of the materials used on all the apparatus, so that the cost of the paraminophenol hydrochloride produced with the emergency equipment described was considered too high to compete with any chemical process. When intermediates became available therefore for the chemical process of preparation the electrolytic manufacture of paraminophenol was abandoned. Some work was done on the use of the anode chamber for the electrolytic production of persulphates simultaneously with the reduction at the cathode to reduce the cost, but these experiments were not considered promising and the plant was finally converted entirely to the production of ammonium persulphate during the period that this chemical was in demand by the government.

DISCUSSION.

A MEMBER: I would like to ask whether any effort was made to keep the benzine in a better emulsified condition than possible in the type of cell described?

A. S. MCDANIEL: Yes, we made attempts to work with emulsions, but under the emergency we felt that the results could be obtained more quickly by dissolving the nitro benzine and keeping it in solution in fairly strong sulphuric acid in which it is fairly soluble and I think the results bore us out.

A MEMBER: I would like to ask how the laboratory results compared with the expansion?

A. S. MCDANIEL: Well, as usual, we ran into a great deal of difficulty, of which I recall one instance. Unexpected difficulties confronted us. We designed a laboratory cell and analyzed the method into all the factors that we could think of, and then in enlarging, we tried to keep those factors the same, and succeeded, I think in large part, and then we ran into a frothing difficulty which temporarily upset all our calculations.

A MEMBER: I refer more particularly to the relative yields.

A. S. MCDANIEL: No, the yields were somewhat less on large scale production, perhaps 10 percent.

A MEMBER: What prompted that question was, by using a device on a laboratory scale in which we had been able to keep a very uniform emulsion, we had run our current efficiency up to 97 percent and our chemical yield up to about 94 percent.

Our laboratory study indicated that an essential to high chemical yield of the complete emulsification of the nitro benzine in the dilute acid is keeping the electrolyte as nearly uniform as possible. I think we have proved, at least to our own satisfaction, that the frothing is caused by the production of azo bodies there which subsequently decomposed.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

SOME ASPECTS OF ELECTROLYTIC IRON.

By W. Albert Noyes, Jr.[1]

The importance attached to electrolytic iron from a commercial standpoint has led to numerous investigations as to suitable electrolytes, and as to the effect of temperature and current density upon the nature of the deposit and the efficiency. It is useless to present an extended outline of all of this work at the present time. Guillet[2] gives a fairly comprehensive resumé of the work on the subject up to 1915. Some of the more important recent researches have been carried out by Vié[3] and by MacFadyen,[4] although some of their results are scarcely consistent with previous work.

At the present time practically the only commercial manufacture of electrolytic iron is carried on at Grenoble, France. A revolving cathode is employed, together with ferric oxide as a depolarizer.[5] Further facts as to the process are not given, except that a temperature of 80° C. is employed and the yield per kilowatt year (including the power used for turning the cathodes) is two metric tons.

Various theories of galvanic polarization have been very fully discussed in chemical literature, and it is useless to mention them further at the present time. Langmuir[6] discusses the theories on the basis of the electron theory, but it is not intended here to enter so much into the general theories on the subject as to treat of certain phases more closely related to electrolytic iron.

[1] This work formed part of a thesis submitted to the Faculty of Science of the University of Paris in partial fulfillment of the requirements for the degree of Doctor of Science. Certain parts have appeared in Comptes Rendus, see (1919), **168**, 1049; **169**, 971; (1920), **170**, 177. Manuscript received November 24, 1920.

[2] Rev. de Met. (1915), **12**, 87.

[3] Ann. Chim. Anal. et Chim. App. (1919), **1**, 175.

[4] Trans. Faraday Society (1920), **15**, 98.

[5] Guillet, *loc. cit.*

[6] J. Am. Chem. Soc. (1919), **41**, 877; Trans. Am. Electrochem. Soc. (1916), **29**, 125.

Experimental.

The first object of the present research was to measure the minimum potential at which the electrolytic deposition of iron could be carried out. It is a well-known fact that iron exhibits passivity phenomena, and an iron anode frequently appears to be practically insoluble during electrolysis. Here again we find much work in the literature, and it is useless to present a theoretical discussion here.

Coehn and Dannenberg,[7] using an anode of platinum, measured the cathodic deposition potential of iron at ordinary temperatures and obtained the value of approximately 0.64 or 0.65 volt. One purpose of this investigation was to measure the voltage in

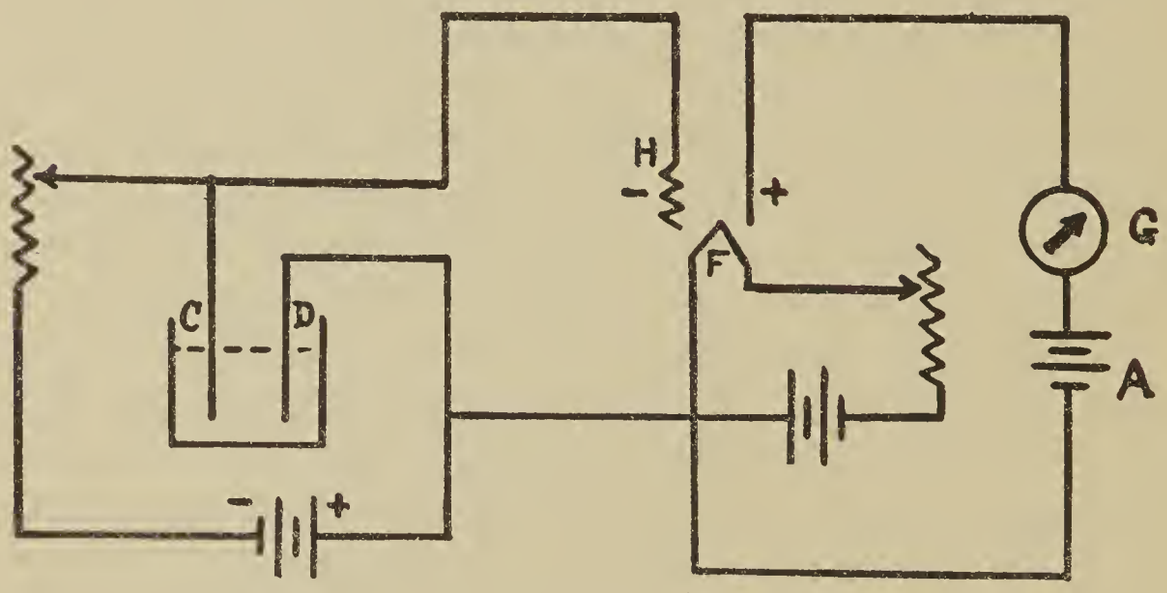


Fig. 1.

aqueous solutions at which transfer of the iron from the anode to the cathode actually commenced, and for this purpose voltage was plotted against current. In order to eliminate errors due to having a measuring instrument shunted across the cell, the following device was used:

The two electrodes C and D (Fig. 1) were thus attached: the positive to the common circuit end of the filament, F, the negative to the grid, H, of an ordinary French army type three-element vacuum tube. In order that the slight variations in grid potential should produce large enough variations in the galvanometer of the plate circuit G, it was necessary to choose the proper value for the plate potential, A. After several trials it was found that a

[7] Z. Phys. Chem. (1901), 38, 609; Z. Elektrochem. (1901), 7, 1095.

plate potential of between two and four volts was satisfactory. Since absolute values were not necessary in reading the current passing through the electrolyte, an ordinary milliammeter was used for the purpose.

Since small changes in the filament current produced relatively large variations in the plate current, some trouble was experienced in calibrating the vacuum tube with sufficient accuracy. A constant value of the filament current when read by ordinary measuring instruments seemed insufficient for the purpose. This error was, however, eliminated as follows: Before each reading, the common circuit end of the filament and the grid were connected together and the plate current galvanometer G, was read. Then, before making the calibration, this "zero" was duplicated by varying the filament current.

TABLE I.

Iron Solution: ½ Molal $FeCl_2$		Nickel Solution: ½ Molal $NiCl_2$	
Temperature of Electrolyte	Potential for Electrolysis	Temperature of Electrolyte	Potential for Electrolysis
20° C.	0.66 Volt	20° C.	0.60 Volt
30° C.	0.60 "	41° C.	0.45 "
50° C.	0.45 "	59° C.	0.38 "
75° C.	0.33 "	96° C.	0.24 "
102° C.	0.14 "	106° C.	0.21 "
109° C.	0.13 "	120° C.	0.17 "
122° C.	0.13 "	130° C.	0.15 "
156° C.	0.18 "	153° C.	0.13 "
182° C.	0.23 "		

Since the current from the filament to the plate in the bulb depends on the emission of electrons from the heated filament, the grid-filament current was rendered negligible by giving the grid a negative potential. For the range used, however, the plate current was practically a linear function of the grid potential. The observations were as shown in Table I, which gives two series of results, for nickel and for iron. The plates, in the case of iron, were of electrolytic iron, heated to drive out the occluded hydrogen; in the case of the nickel they were of nickel which was, by analysis, 99.4 percent pure. The solutions were half molal in

each case. The values are obtained by plotting current against voltage, and observing the sharp angle when the current begins to increase rapidly with increase in voltage. Care was taken to exclude oxygen, and each value is the average of several determinations.

A glance at the results will show that iron passes through a minimum while nickel (which is here given only for comparison) does not. The values for nickel below 75° agree well with those given by Schildbach,[8] but those for iron fall off much more rapidly than those given by Mustad.[9] This fact is rather difficult to explain, but we may obtain some light on the subject by considering the percentage attack of anodes at 18° and at 48° in normal ferrous chloride as a function of the voltage. See Table II.

TABLE II.

Solution: ½ Molal $FeCl_2$.

18° C.		48° C.	
Voltage	Attack, percent of Theory	Voltage	Attack, percent of Theory
0.70	0	0.39	10
0.80	83	0.48	100
0.96	88	0.76	100
1.18	95	0.98	89
1.43	95	1.41	84
1.70	78	1.85	76

The figures show that the anode attack begins at a relatively lower voltage at higher temperature, and therefore we should expect the potential drop for deposition to decrease. At higher voltages the attack again decreases, without doubt due to the liberation of oxygen.

Referring again to the results in Table I, it is difficult to offer a satisfactory explanation of the fact that iron passes through a minimum toward 110° while nickel does not. The first possibility is that this would be due to the hydrogen ions present, but the curve for separation potential of sulphuric acid exhibits no minimum.[10] The minimum might also be ascribed to oxidation

[8] Z. Elektrochem. (1910), **16**, 967.
[9] Abhdlg. d. Bunsen Ges. (1909), **2**.
[10] Comptes Rendus (1919), **168**, 1049.

of the iron, but precautions were taken to reduce this to a minimum.

Table III gives some measurements of polarization potentials in a solution of ferrous sulphate (25.1 grams of iron per liter). The electrodes were of steel (0.8 percent carbon) over which had been deposited a thin layer of electrolytic iron. The electrolyte was at first acidified with a little sulphuric acid and some pieces of electrolytic iron placed in the bottom of the cell. Nitrogen (carefully freed from all traces of oxygen by means of passing

TABLE III.

Temperature	Polarization	Electrode	Solution
14.9° C.	0.278 Volt	Cathode	Slightly acid
55° C.	0.208 "	"	" "
74° C.	0.127 "	"	" "
14.9° C.	0.037 "	Anode	" "
55° C.	0.005 "	"	" "
15.0° C.	0.209 "	Cathode	Neutral
15.0° C.	0.219 "	Anode	"

Current Density	Polarization	Temperature	Electrode
0.0046 amp. sq. cm.	0.038 Volt	12.0° C.	Cathode
0.0220 " " "	0.087 "	12.0° C.	"
0.0041 " " "	0.143 "	12.0° C.	Anode
0.0116 " " "	0.251 "	12.0° C.	"

over heated copper turnings) was then bubbled through the solution continuously, a slight excess pressure of nitrogen was always maintained to prevent the entrance of oxygen. The solution showed no trace of ferric iron either before or after the measurements, and it was neutral to litmus.

The voltage of the iron electrode was balanced against a hydrogen electrode. The platinum was carefully platinized, using the precautions of Ellis[11] and the average for the voltage Fe-$FeSO_4$-H was 0.428, although the object of the experiment was to measure the variation of this potential after breaking the current between

[11] J. Am. Chem. Soc. (1916), 38, 742.

two iron electrodes. The polarization was practically a linear function of the current, although variations were only appreciable in the neutral solution.

If we consider the osmotic formula for the potential of an electrode traversed by a current, we note that the curve obtained by plotting the potential against the logarithm of the current should be a straight line. Several authors[12] have shown that in the case of liberation of a gas at the electrode, this is approximately the case, but it is usually found that the slope of the line can not be calculated from Nernst's formula.

This formula is based on two principal suppositions:

1. That the rate of formation of active material is proportional to the current density;

2. That its rate of decomposition is proportional to its partial pressure.

Lewis and Jackson[13] point out that the most probable reason for the discrepancy between the theoretical values and those found is that the reaction probably does not take place in a homogeneous phase.

In a separate set of experiments, the results of which are not given, the potential of an iron electrode was measured against that of a normal zinc electrode, and plots were obtained of the log current-potential values at different temperature. The lower part of the curve in each case was a straight line, the slope of which could be approximately calculated from the formula $S = \frac{0.0002T}{3/5}$ instead of $S = \frac{0.0002T}{2}$ by Nernst's formula. Table IV gives a summary of these results:

TABLE IV.

Calculated Slope	Experimental Value	Temperature
0.0960 Volt	0.0966 Volt	14.5° C.
0.1098 "	0.1090 "	56.5° .C.
0.1134 "	0.1130 "	67.5° C.

[12] Lewis and Jackson, Proc. Am. Acad. (1906), **41**, 406; Jahn und Scoenrock, Z. Phys. Chem. (1895), **16**, 45; Usher and Venkateswaran, J. Chem. Soc. (1919), **115**, 613.

[13] Lewis and Jackson, *loc. cit.*

Since the part of the curve which conforms to the above equation is relatively small, and owing to the fact that heretofore only cases involving gases have been found to show like agreement, hydrogen is probably liberated at lower voltages. As the temperature increases the part of the curve which is a straight line becomes shorter, which is entirely in agreement with Ghosh's[14] conclusion that the phenomenon of "overvoltage" has disappeared at 96° C.

In acid solution the anode polarization is practically negligible, which agrees with Foerster's[15] view that a slight liberation of hydrogen on an iron electrode will render it "active." When the electrode was placed in the solution, a minute quantity probably dissolved in the acid with liberation of hydrogen and the "passivity" of the anode was thereby decreased. The coefficients for variation of separation potential with the temperature are of the same order of magnitude as the coefficients of polarization found by Jahn,[16] but the coefficients for polarization are considerably smaller than his.

In conclusion, I wish to express my indebtedness to Prof. Henry Le Chatelier for the facilities placed at my disposition and the general guidance of my work, and also to Dr. Charles Marie for many valuable criticisms and helpful suggestions.

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University of Paris,
France.

DISCUSSION.

WM. BLUM[1]: Without discussing this particular paper on electrolytic iron, I think it is worth while to call attention to a new development in the electrodeposition of iron. During the war Great Britain used in the repair depots in France iron deposition

[14] J. Phys. Chem. (1917), **21**, 426.
[15] Foerster, Elektrochemie wässriger Lösungen (1915), 372
[16] Z. Phys. Chem. (1895), **18**, 399.
[1] Chemist, Bureau of Standards, Washington, D. C.

very successfully for building up worn and undersized parts. Any one interested in that will find this described in an article by McFayden in the Transactions of the Faraday Society (1920, **15**, 98).[2] I mention that because recently there has been interest expressed by the automobile manufacturers as to how they can bring up worn crankshafts, etc., by depositing iron on them.

[2] Reference to this article given on first page of this paper.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

THE USE OF FLUORIDES IN SOLUTIONS FOR NICKEL DEPOSITION.[1]

By William Blum.[2]

Abstract.

Discusses the factors governing the deposition of hard deposits of nickel from solutions containing fluorides, with and without boric acid and other salts. The general principles of getting good deposits are discussed, showing that low acidity favors good nickel deposition, but high acidity good anode corrosion. The bearing of hydrogen ion concentration on the matter is explained. The effect of additions, such as boric acid, is probably through their effect on hydrogen ion concentration. Deposits of finer structure and higher tensile strength are obtained from fluoride solutions than from the corresponding chloride solutions.

[J. W. R.]

I. INTRODUCTION.

In connection with a process for the electrolytic reproduction of engraved printing plates, recently installed at the Bureau of Engraving and Printing under the supervision of the Bureau of Standards, it was necessary to secure for the printing surface nickel coatings which would be as hard as possible, but at the same time free from brittleness or a tendency to curl. In connection with this process the addition to nickel solutions of hydrofluoric acid or fluorides, recently recommended by E. G. Lovering, was investigated. The beneficial effect of such additions upon the physical properties of the deposited nickel was found to be so great that this type of solution was adopted and has been

[1] Published by permission of the Director of the Bureau of Standards. Manuscript received March 14, 1921.

[2] Electrochemist, Bureau of Standards, Washington, D. C.

used successfully in the above-mentioned plant. The necessity for selecting and controlling conditions which would permit immediate application of the process has prevented any exhaustive investigation of the principles involved. However, the observations made and results thus far obtained may be of interest and may serve to promote discussion and further study of the subject.

II. HISTORICAL.

As the nickel solutions employed usually contain boric acid, we may assume that upon the addition of fluorides, fluoborates are formed. The use of fluoborate solutions for plating was first proposed by Leuchs,[3] who made experiments with several metals, but not with nickel. In 1908 Kern and Fabian[4] employed a nickel fluoborate solution, from which they secured a thick deposit (5/16 inch = 8 mm.) having desirable physical properties. About the same time, O. P. Watts[5] and his associates made a few experiments with nickel solutions containing fluoborates and also secured promising results. In 1912 they found that good deposits could be secured from nickel fluoride solutions containing free hydrofluoric acid. In the same year A. Hollard[6] experimented with a nickel fluoborate solution for making electrotypes. So far as known to the author, however, no commercial application of nickel solutions containing fluorine was made until recently, when E. G. Lovering,[7] of Detroit, operated plating solutions containing in addition to the usual constituents, *viz.*, nickel sulphate and boric acid, small amounts of hydrofluoric acid. He obtained such remarkable results that he designated hydrofluoric acid as the "magic fluid." Subsequently F. J. Liscomb[8] published the results of a few experiments in which he employed solutions of nickel fluoborate and nickel-ammonium fluoborate, from both of which he obtained only fairly satisfactory deposits.

Publication and discussion of Lovering's results caused numerous electroplaters to try the use of hydrofluoric acid in nickel

[3] German Patent 38,193, May 13, 1886.
[4] School of Mines Quarterly (1908), **29**, 367.
Trans. Amer. Electrochem. Soc. (1909), **15**, 464.
[5] Monthly Review, American Electroplaters' Society, March, 1921.
[6] Bull. Soc. d'Encour. (1912), p. 24.
Brass World (1912), **8**, 391.
[7] Monthly Review, American Electroplaters' Society, Feb., 1920.
[8] Brass World (1920), **16**, 311.

baths, with thus far somewhat contradictory results, owing in part, no doubt, to failure to define or control all of the conditions employed by them. Even though very marked effects are produced by the fluorides in the presence of boric acid, there is no reason to believe that such solutions form a panacea for all the ills of the plater. Just as the studies of cobalt plating several years ago led to important improvements in nickel plating, the investigation of fluoride nickel solutions may throw light on the behavior of the nickel solutions more commonly used, and may thereby lead to their improved operation.

III. GENERAL PRINCIPLES.

If hydrofluoric acid is added in small amounts to a nickel bath, the acidity thus produced will cause an increase in anode efficiency and a decrease in cathode efficiency, and at least a partial neutralization of the hydrofluoric acid, to form either nickel fluoride, or in case boric acid is present, a fluoborate. Since good nickel deposits cannot be secured from solutions which are appreciably acid, the solution must be operated for some time after the addition of hydrofluoric acid, or the bath must be neutralized, before satisfactory results are obtained. It therefore appears more logical to neutralize the hydrofluoric acid before adding it to the bath.

In order to produce baths of relatively simple composition the fluorine was first added in our experiments in the form of nickel fluoride, prepared by the solution of nickel carbonate in hydrofluoric acid. When commercial nickel carbonate in excess is treated with 5 *N* hydrofluoric acid a solution is obtained which contains only about 80 per cent. of the amount of nickel equivalent to the hydrofluoric acid used. It is evident, therefore, that in such solutions there is a tendency to form acid fluorides. With freshly precipitated nickel carbonate, neutralization is more rapid and more nearly complete, but in no case is a neutral solution obtained. This observation is in general accord with the experiments of F. H. Edminster and H. C. Cooper,[9] who found that if hydrofluoric acid is neutralized with nickel carbonate the definite crystals obtained by several recrystallizations have the formula

[9] Jour. Amer. Chem. Soc. (1920), 42, 1419.

$NiF_2.5HF$, although there is a tendency to form crusts having approximately the composition NiF_2. For simplicity we may assume that the solution contains nickel fluoride, NiF_2, and a small excess of hydrofluoric acid.

If now boric acid in excess is added to such a solution, a precipitate, which probably consists of nickel hydroxide, separates, and the resultant solution contains nickel in the ratio of approximately 1Ni to 4F. About the same ratio is obtained if the hydrofluoric acid and boric acid are first mixed and the resultant "fluoboric acid" is neutralized with nickel carbonate. It is difficult to assign a formula to the "fluoborate" which probably exists in such a solution. If we assume the simplest formula for fluoboric acid *viz.*, HBF_4, we would expect the formation of nickel fluoborate having the formula $Ni(BF_4)_2$, *i. e.*, with 1Ni to 8F. To produce such a compound by reaction between nickel fluoride and boric acid would require a reaction such as the following:

$$4NiF_2 + 2H_3BO_3 = Ni(BF_4)_2 + 3Ni(OH)_2.$$

The reaction which actually occurs is apparently similar to this, but no doubt less simple, and the salt formed is a more complex fluoborate. Hollard[10] used hydrofluoric acid and boric acid in proportions to yield a solution approximately 0.8*N* in HBF_4 and 0.2*M* excess H_3BO_3, and agitated the solution for 20 hours with freshly precipitated nickel carbonate to secure complete neutralization, but did not record the nickel concentration of the resultant solution. As pointed out in a paper on lead fluoborate solutions[11] there is a great need for study of the constitution of fluoboric acids and fluoborates.

In view of the uncertainty as to the constitution of the nickel fluoborates which are almost certainly present in these solutions, it is most satisfactory to express the composition of the solutions employed in terms of the amount of the constituents actually used in their preparation. Thus if a solution is stated to be 1.8*N* in nickel sulphate, 0.2*N* in nickel fluoride and 0.5*M* in boric acid, it was prepared by treating an amount of hydrofluoric acid equivalent to a final concentration of 0.2*N*, with an excess of nickel car-

[10] *Loc. cit.*

[11] Trans Amer. Electrochem. Soc. (1919), **36**, 243

bonate, and after all reaction had ceased, by adding the requisite amount of boric acid. This mixture was added to the nickel sulphate solution, and thoroughly mixed. After standing for several hours, the solution was filtered. By this method of preparation the solutions were made as nearly neutral as possible, as they were at all times in contact with nickel carbonate and nickel hydroxide. This procedure was employed at first because it was desired to obtain solutions containing no other metal than nickel. As will be explained later, it is far simpler to prepare solutions by the use of sodium fluoride, which solutions are very similar in behavior to those made from nickel fluoride.

IV. METHODS OF ANALYSIS AND CONTROL.

For satisfactory experimentation or commercial application of plating solutions, it is essential to have reliable methods of analysis. In solutions containing nickel, fluorides and boric acid there is no difficulty in determining the nickel content by the usual electrolytic methods. The estimation of fluorine and of boric acid is, however, very difficult, and at present we know of no entirely satisfactory methods for fluorine, and no methods whatever for the boric acid in such solutions.

The determination of fluorine by precipitation as calcium fluoride is at best a tedious method, owing to the difficulty of retaining the calcium fluoride upon a filter. If calcium carbonate, or, as has recently been proposed, calcium oxalate,[12] is precipitated along with the calcium fluoride, the precipitate may be retained on a filter, but the filtration and washing still require a long period. In order to apply such a method to the plating solutions it would be necessary to remove the sulphate, and moreover the presence of boric acid would cause uncertainty in the composition of the final precipitate. These difficulties were found to be so great that after numerous attempts the gravimetric estimation of fluorine in these solutions was abandoned.

Approximate results have been obtained by a simple volumetric method which was first proposed by A. Greeff.[13] It depends upon titration of the neutral fluoride with standard ferric

[12] Edminster and Cooper, *loc. cit.*

[13] Ber. d. Deutsch, Chem. Ges. (1913), **46**, 2511.

chloride solution, which forms a precipitate having the formula Na_3FeF_6 analogous to cryolite. In order to repress the solubility of this salt, sodium chloride is added in large excess. Sodium sulphocyanate is used as the indicator and a layer of ether is employed to extract and concentrate the ferric sulphocyanate formed when the ferric chloride is present in slight excess. The end point is reached when a permanent faint pink color is produced in the ethereal layer. The details for the application of this method to nickel solutions have not yet been perfected, but the indications are that the method will be sufficiently accurate for plant control.

Of even greater importance than the determination of the major constituents of a nickel-depositing solution are the estimation and control of the acidity, or, more strictly speaking, of the hydrogen ion concentration of the solution. In nickel deposition in general and especially in the accurate reproduction of engraved plates, the most common difficulties encountered are (1) "pitting" and (2) "cracking" or "curling." Even though there may be other contributing factors, it seems reasonably certain that the principal cause of such defects is excessive acidity of the solutions, or at least excessive liberation of hydrogen at the cathodes. In discussing the cause of pits it is necessary to distinguish between them and projections, which latter are usually initiated by the presence in the solutions of suspended conducting particles such as nickel and carbon derived from the anodes. Before any really conclusive evidence can be obtained, however, as to the cause and prevention of pitting and cracking, means must be secured for measuring and controlling the acidity of such solutions.

The hydrogen ion concentration of a solution may be expressed directly in the following form: $(H^+) = 10^{-6}$; which signifies that the actual concentration of hydrogen ions in the solution is $\frac{1}{1{,}000{,}000}$ normal. In order to avoid the use of the negative exponent, S. P. L. Sörensen[14] employed the log $\frac{1}{(H^+)}$, to which value he applied the expression pH. Thus in the above case pH = 6. In using this method of expression it is necessary to

[14] Compt. rend. Lab. Carlsberg (1909), 8, 1.

bear in mind that a large numerical value for pH represents a low hydrogen ion concentration or acidity, and *vice versa.* A detailed discussion of methods of measuring and expressing the hydrogen ion concentration will be found in a recent book by W. M. Clark.[15] Throughout this article the pH values will be employed.

Various methods for testing the acidity of nickel plating solutions have been proposed and employed to advantage in plant control. The simplest is the testing of the solution with litmus and congo-red papers which, it is frequently claimed, should both be turned pink by a solution in good operating condition, *i. e.,* the solution should be acid to litmus and alkaline to congo-red. In measurements depending upon the actual titration of nickel solutions the most common indicator thus far employed is sodium alizarin-sulphonate. A solution is said to be satisfactory if a given sample requires a certain amount of acid or of alkali to produce a neutral (or some definite) tint with this indicator.

These two methods illustrate the measurement of two distinct factors in the acidity of such a solution, *viz.,* the intensity and the quantity factor. The first method measures, at least roughly, the hydrogen ion concentration; the second determines the amount of acid or of alkali required to produce some definite hydrogen ion concentration. Either method may be useful, but both are necessary to a complete understanding of the behavior of such a solution during operation.

The application of hydrogen ion measurements should prove very valuable in determining not only the optimum range of acidity for nickel deposition, but also the possible function of various additions, such as fluorides and boric acid, in regulating this acidity. In such measurements it is important to determine not alone the pH of solutions of certain composition, but also the rate at which the pH changes upon the addition of acid or alkali, since this rate determines the degree to which the solution will automatically compensate for any variation in anode or cathode efficiency. So far as acidity is concerned, the ideal nickel plating solution is one which will within the desired working range have a relatively flat neutralization curve; in other words, it should be a

[15] The Determination of Hydrogen Ions, Williams and Wilkins, Baltimore, Md., 1920.

well "buffered" solution. Much work remains to be done on this subject, as it will require the laboratory study of many solutions and the correlation of such results with the operation of corresponding baths over long periods. The observations thus far made by us are distinctly preliminary.

Since the hydrogen ion concentration of these solutions appears to be directly related to their behavior upon electrolysis, attempts were first made to measure this property by means of the hydrogen electrode. Even with pure nickel sulphate solutions, however, the results were not consistent or reproducible. Frequently values would be obtained which appeared to be definite, but with another electrode appreciably different values were secured. The results were still less reliable when the commercial plating solutions were thus tested. This latter difficulty is probably attributable to the presence in commercial solutions of small amounts of copper, iron or arsenic, which may "poison" the electrodes. The difficulty with pure nickel sulphate cannot be readily explained. The only conclusion that could be reached from hydrogen electrode measurements conducted at different times during the past several years is that normal nickel sulphate solution has a pH value between 6 and 7, *i. e.,* the hydrogen ion concentration (H^+) is between 10^{-6} and 10^{-7}; and that satisfactory plating solutions have a pH value between 4 and 6.

More satisfactory results have been obtained by measuring the hydrogen ion concentration with indicators, using the "drop method" as proposed by L. J. Gillespie[16] and also described in detail by W. M. Clark.[17] In this method, instead of preparing hydrogen ion standards by the use of buffered salt solutions, tubes containing different fixed proportions of the given indicator in its acid and alkaline form are placed in pairs so that the color observed by transmitted light is that of a partly transformed indicator, corresponding to some known pH. When the test solution is colored, as with nickel solutions, it is necessary to include in each series of standards a third tube containing the nickel solution. A definite quantity of indicator is then added to a separate portion of the nickel solution, two tubes containing water are placed in series with it, and the resultant color is

[16] Jour. Amer. Chem. Soc. (1920), 42, 742.

[17] "The Determination of Hydrogen Ions," by W. M. Clark (Williams and Wilkins, 1920).

matched against the indicator color standards as above prepared. The indicators which have been found most useful in measurements upon nickel solutions are brom-phenol blue, and brom-cresol purple, which together cover the range involved, *i. e.*, pH = 3.5 to 7.0. At first methyl red appeared to be well suited for this purpose, since it is very sensitive in the region from pH = 4.0 to 6.0; but careful measurements showed that in nearly neutral nickel solutions anomalous results are obtained with this indicator, presumably because of some specific salt effect. Preliminary observations with indicators show that the pH of normal nickel sulphate solutions is about 6.8, and that the addition of even very minute amounts of acid causes a great increase in acidity, that is a decrease in pH.

In Fig. 1, *A* is a typical "titration curve" of nickel sulphate, *i. e.*, it represents the changes in hydrogen ion concentration produced by successive additions of acid or of alkali. This curve, based on measurements with indicators, has the same shape and approximately the same position as one which was obtained with the hydrogen electrode, in which latter case, however, the readings were somewhat uncertain and erratic. The large effect upon the hydrogen ion concentration produced by the addition of small amounts of sulphuric acid to nickel sulphate solutions indicates clearly why it is not practicable to deposit nickel from a solution containing only nickel sulphate, as even slight deficiency in anode corrosion will result in such a large increase in hydrogen ion concentration as to cause a low cathode efficiency and a poor deposit. Bennett [18] and his associates found that the cathode efficiency in a "neutral" nickel ammonium sulphate solution was low, but that by the addition of small amounts of ammonia to the solution the cathode efficiency approached 100 percent. They did not however make any measurements of the change in hydrogen ion concentration thus produced.

The effect of boric acid in maintaining a uniform slight acidity of a nickel bath is shown in Curve *B* of Fig. 1. Let us assume, as a first approximation, that a satisfactory nickel bath should have a pH between 4 and 6 (actually the range may be much narrower). By comparison of curves *A* and *B*, it is seen that in 50 cc. of a

[18] C. W. Bennett, H. C. Kenny and R. P. Dugliss. Trans. Amer. Electrochem. Soc. (1914), **25**, 335.

normal nickel sulphate solution it requires less than 0.5 cc. of 0.2*N*. NaOH to change the pH from 4 to 6, whereas, in the solution containing boric acid it requires about 2.5 cc. of the alkali to produce the same change in pH. This observation confirms the

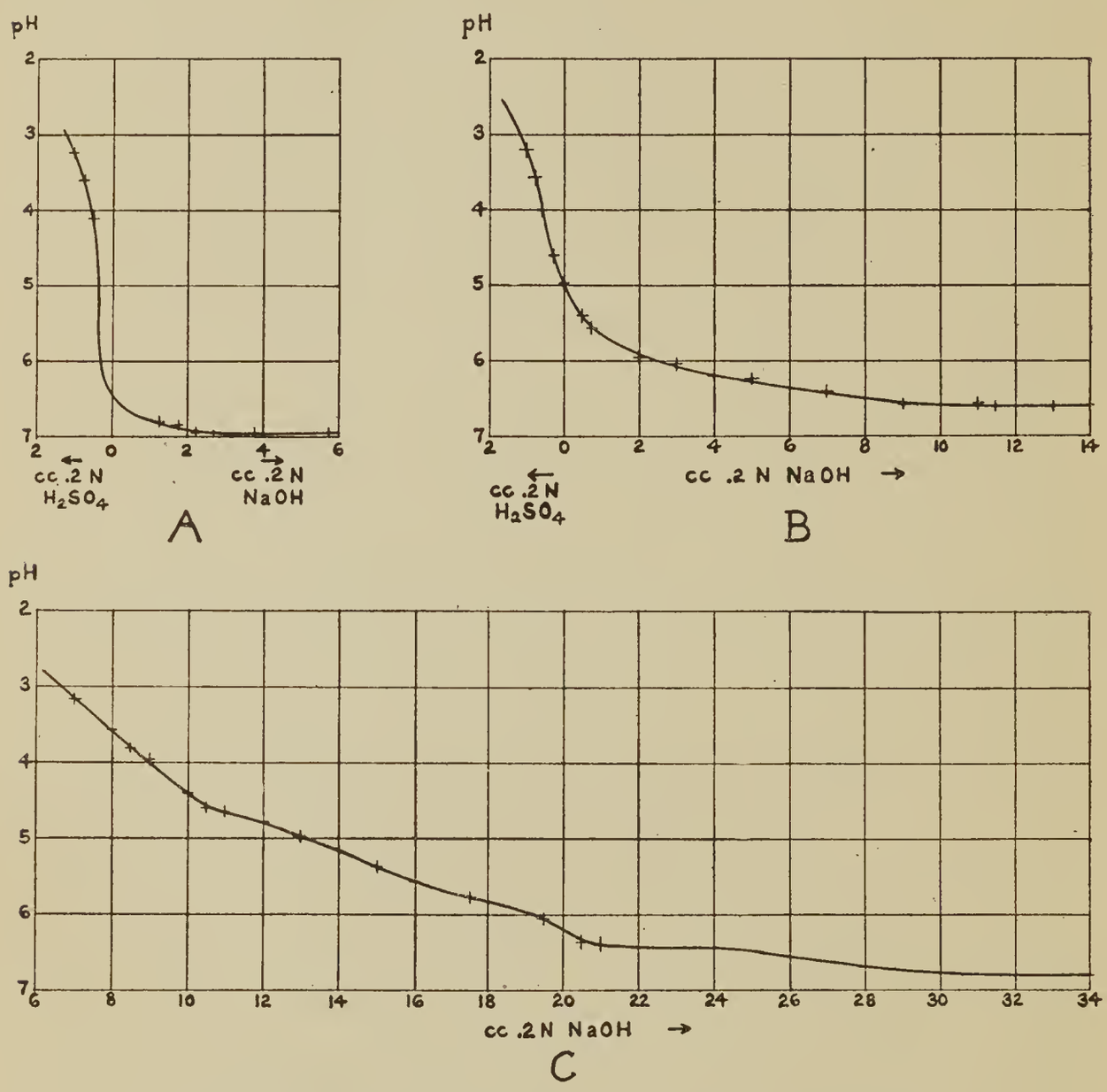


FIG. 1. Hydrogen Ion and Neutralization Curves of Nickel Solutions. Based on colorimetric measurements upon 50 cc. of solution.

Initial Composition:

A: $NiSO_4$ — *N*.
B: $NiSO_4$ — *N*; H_3BO_3 — 0.5*M*.
C: $NiSO_4$ — *N*; H_3BO_3 — 0.5*M*; HF — 0.1*N*.

conclusion of L. D. Hammond[19] that the principal function of boric acid in nickel baths is the maintenance of a uniform low hydrogen ion concentration. Upon reversal of the neutralization process, *i. e.*, the addition of acid to a solution made slightly alkaline with sodium hydroxide, a curve of similar shape is obtained.

[19] Trans. Amer. Electrochem. Soc. (1916), **30**, 103.

If, however, nickel hydroxide has been actually precipitated by the alkali, there is a certain "lag" in its solution by the acid, which causes the solution at any stage to be more acid (a lower pH) than corresponds to the true equilibrium. This lag is very much less if boric acid is present, than in the simple nickel sulphate solution.

Curve *C* of Fig. 1 illustrates the effect of the addition of alkali to a nickel solution containing both hydrofluoric and boric acids. It is apparent that the reaction is complicated and that considerable further study will be required to explain the significance of each part of the curve. It is evident, however, that the solution is "well buffered," *i. e.*, the pH does not change as rapidly upon the addition of alkali as it does in the pure nickel sulphate solution or in that containing only boric acid. To produce the same change as above considered, *viz.*, pH = 4 to 6, it requires about 10 cc. of the 0.2*N* alkali, i. e., four times as much as in the solution with boric acid, and over twenty times as much as in pure nickel sulphate solutions. Whether this marked regulating effect of the fluorides or fluoborates is the principal cause of their effect upon the structure of the deposits, must be determined by more exhaustive experiments.

It is significant that in all three curves the pH at the point where nickel hydroxide begins to precipitate (and beyond which the pH changes very slightly until all the nickel is precipitated) is about 6.8, *i. e.*, nearly the same as the neutral point of nickel sulphate. This shows that when these solutions are neutralized by agitation with nickel hydroxide, they all reach the same degree of neutrality. A few experiments indicate that the same pH is obtained by neutralizing the solutions with nickel carbonate.

V. EXPERIMENTS UPON THE OPERATION OF SOLUTIONS.

Most of the experiments upon these solutions were carried out at the Bureau of Standards. Observations were also made upon solutions in operation at the Bureau of Engraving and Printing. Small scale experiments were conducted in glass battery jars containing from 1 to 10 liters and in stoneware tanks with a capacity of about 30 liters. Within short periods there was practically no etching of the glass or stoneware by the solutions

containing fluoborates. For continuous operation it is probably best, however, to line stoneware vessels with a bituminous coating, since it has been found that when lead fluoborate solutions are kept in stoneware for a year or more there is decided etching. For factory operation of these solutions both the stoneware and wooden tanks have been lined with bituminous material. There is no appreciable contamination of the solutions when kept in chemical glassware during analysis.

For purposes of comparison the fluoborate baths were usually run in series with a nickel bath similar to that recommended by O. P. Watts,[20] but in order to permit a ready comparison between the function of the chlorine and fluorine, Watts' formula was slightly modified to yield definite normalities.

TABLE I.

Formula of "Chloride" Solution. Bath No. 2.

		g/L	oz./gal.
Nickel sulphate	1.8 *N*	255	34
Nickel chloride	0.2 *N*	24	3.2
Boric acid	0.5 *M*	31	4.2

A corresponding "fluoride" bath was prepared, of which, however, the composition is not strictly equivalent to that of the chloride bath, since, as previously noted, some nickel hydroxide separates out upon mixing nickel fluoride and boric acid. The constituents actually used in its preparation were as follows:

TABLE II.

Formula of "Fluoride" Solution. Bath No. 3.

		g/L	oz./gal.
Nickel sulphate	1.8 *N*	255	34
Nickel carbonate*		12	1.6
Hydrofluoric acid* (50% HF)		8	1.1
Boric acid	0.5 *M*	31	4.2

* Equivalent to 0.2 *N* nickel fluoride.

[20] Trans. Am. Electrochem. Soc. (1916), 29, 125.

A few preliminary experiments were made with nickel fluoborate without sulphate and with solutions containing 50 percent of the nickel as fluoborate and 50 percent as sulphate; but the deposits obtained were less satisfactory than those with the above solution in which approximately 10 percent of the nickel is present as fluoborate. Most of the studies were therefore conducted with the latter solutions. A few experiments with solutions containing only nickel sulphate and nickel fluoride yielded unsatisfactory deposits.

In general the solution to be studied was run in series with the "chloride" bath and with a copper voltameter (coulometer). In most cases deposition was produced upon polished steel plates which had been treated with sodium sulphide solution to permit subsequent separation of the deposited nickel. Where physical tests of the deposits were to be made, the steel plates were surrounded with a shield of insulating material ("Formica") which served to reduce the current density at the edges and to produce a more uniform current density and thickness over the entire surface. Through use of a shield it was also possible to employ higher average current densities than otherwise, as under ordinary conditions the edges receive an excessive current density and become cracked or "burnt."

Unless otherwise noted, commercial "95-97 percent" cast nickel anodes having an area approximately equal to the cathodes were employed. An analysis of one lot of these anodes[21] yielded the following results:

TABLE III.

Composition of Nickel Anodes.

	Percent
Nickel (+ cobalt)	97.5
Carbon	1.50
Silicon	0.05
Copper	0.20
Iron	0.60
	99.85

[21] By J. A. Scherrer, of this Bureau.

In a few cases commercial anodes having almost the same composition, except that they contained 0.6 percent of tin, were used, with no apparent difference in the operation of the baths.

As our immediate interest was in securing deposits which would withstand severe abrasion, greater attention was paid by us to the physical properties than to the appearance of the deposits. Pending the development of a satisfactory method for measuring hardness, and especially the "abrasion hardness" of thin layers of metal, a few preliminary tensile tests were made[22] upon the assumption that the results would at least indicate the relative hardness of samples of similar material. The following results were obtained upon relatively thick specimens (about 0.75 mm. or 0.03").

TABLE IV.

Physical Properties of Deposited Nickel.

Expt.	Solution	Current Density		Ultimate Tensile Strength		Elongation in 2 in. (5 cm.) Percent
		Amp./dm.²	Amp./sq. ft.	Kg./cm.²	Lb./sq. in.	
1	Chloride No. 2...	1	9	4900	75,000	
2	"	3	28	4900	75,000	8.5
3	"	5	47	5600	80,000	11.0
4	Fluoride No. 3...	1	9	7000	100,000	
5	"	3	28	8200	117,000	2.4
6	"	5	47	9350	133,000	4.8

Accurate determination of the yield points was not found possible, but the few results obtained indicate that there is less difference in the yield point than in the ultimate tensile strength of the nickel from the two solutions. The data in Table III show that there is a great difference in the ultimate tensile strength of the deposits from the chloride and fluoride solutions, which difference is most marked in deposits produced at relatively high current densities. This difference can be readily observed by manual bending of the samples, when it will be found that the fluoride deposits are much stronger and more elastic than the chloride. It has not been possible to secure any absolutely conclusive evidence of the relative wearing qualities (*e. g.*, on a printing press) of the two grades of nickel, but all the evidence

[22] By L. B. Tuckerman, of this Bureau.

secured confirms the superiority of the fluoride deposit for this purpose.

That this difference in physical properties is accompanied by differences in crystal structure is evident from Fig. 2, from which it will be seen that the deposit from the fluoride is much finer grained than that from the chloride solution. One of the most characteristic differences in the operation of baths containing chlorides and fluorides is the fact that much sludge is produced in the chloride solution, while the fluoride remains practically clear. Under these conditions we would expect a higher content of metallic impurities in the fluoride deposit than in the chloride, in fact the presence of such impurities has been suggested as a cause of the finer crystal structure and higher tensile strength of the fluoride deposit. Analysis of the deposits[23] yielded the results shown in Table V.

TABLE V.

Composition of Deposited Nickel.

	"Chloride" Percent	"Fluoride" Percent
Nickel (+ cobalt)	99.60	99.40
Iron	0.27	0.45
Copper	0.09	0.15
	99.96	100.00

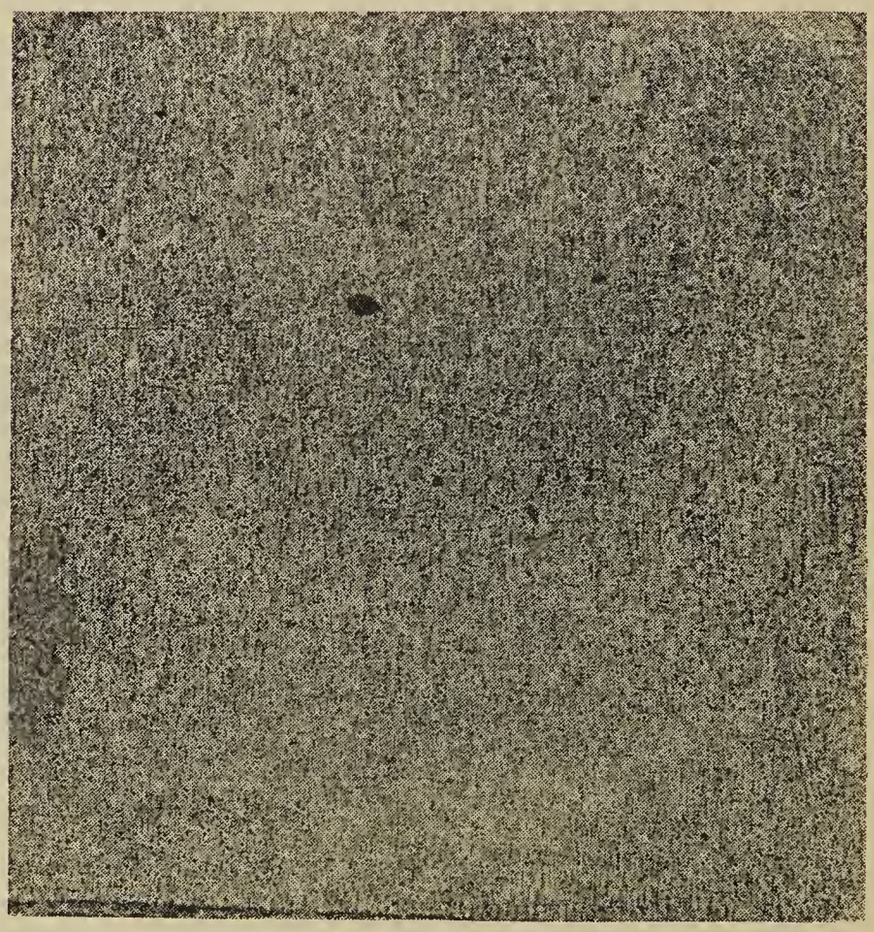
Even though there is a greater content both of copper and iron in the fluoride deposit (approaching closely that present in the anodes), it is at least doubtful whether these amounts of impurities could account for the difference in structure and physical properties, especially since they are present in at least comparable amounts in the chloride deposit. Further experiments are needed to determine whether the effect of the fluorides or fluoborates is specific, or whether similar effects may be produced by other substances.

In view of the good anode corrosion in the fluoride solutions, and the almost complete absence of sludge, a few attempts were made to employ either hot-rolled or electrolytic nickel anodes.[24]

[23] By J. A. Scherrer, of this Bureau.

[24] Furnished for this purpose by the International Nickel Co.

A—"Chloride" Solution—5 amp./sq. dm. (47 amp./sq. ft.)



B—"Fluoride" Solution—5 amp./sq. dm. (47 amp./sq. ft.)

FIG. 2. Structure of Electro-deposited Nickel x 100.

These experiments indicated that the fluoride solution corrodes the hot rolled anodes about as readily as it does the cast anodes, but that the corrosion of the electrolytic anodes is poor until the solution becomes so acid that a very low cathode efficiency is secured. Further work will be required to determine whether the commercial use of rolled anodes in these solutions will prove practicable and economical.

The rolled anodes used in these experiments had the following composition:[25]

TABLE VI.

Composition of Hot Rolled Nickel Anodes.

	Percent
Nickel	98.50
Iron	0.64
Copper	0.17
Carbon	0.05
Manganese	0.35
	99.71

In both the chloride and fluoride solutions it was found that the cathode efficiency for current densities up to 2 amp./dm^2 (19 amp./sq ft.) is above 99 percent. At higher current densities the cathode efficiencies are slightly lower in the chloride than in the fluoride solutions. It is possible to use higher current densities in the fluoride than in the chloride solutions, without producing appreciable cracking or curling of the deposit. Thus on polished brass plates about 6 x 9 cm. (2.5 x 3.5 inches) good adherent deposits were obtained from both solutions at an average of 2 amp./dm^2 (19 amp./sq. ft.), while at 4 amp./dm^2 (37 amp./sq. ft.) the deposit from the fluoride was almost perfect, and that from the chloride was badly curled. These data are of only relative value, however, as the actual current density upon the edges, where cracking first occurred, was certainly much higher than the above values. The deposits referred to in Table IV as secured at a current density of 5 amp./dm^2 (47 amp./sq. ft.), were rendered possible only by the use of the shields.

[25] Analysis by J. A. Scherrer.

As for the immediate purpose in view it was necessary to use wax for insulating purposes, the use of solutions at appreciably elevated temperatures was prevented. All of the experiments herein described were made with solutions at room temperature (20° to 25° C., or 68° to 77° F.). The effects of bath temperature upon the deposits will be included in the further investigations now in progress.

TABLE VII.

Resistivity of Nickel Solutions.

No.	Composition		Resistivity Ohms per cm. cube
1	$NiSO_4$	2.0 *N*	20.5
2	$NiSO_4$ $NiCl_2$ H_3BO_3	1.8 *N* 0.2 *N* 0.5 *M*	19.8
3	$NiSO_4$ NiF_2 H_3BO_3	1.8 *N* 0.2 *N* 0.5 *M*	21.9
4	$NiSO_4$ NiF_2 H_3BO_3 Na_2SO_4	1.8 *N* 0.2 *N* 0.5 *M* 0.5 *N*	17.2
5	$NiSO_4$ NiF_2 H_3BO_3 $MgSO_4$	1.8 *N* 0.2 *N* 0.5 *M* 0.5 *N*	20.9
6	$NiSO_4$ NaF H_3BO_3	2.0 *N* 0.2 *N* 0.5 *M*	19.9

One of the important factors in the operation of plating solutions is the conductivity, because an increase in conductivity not only represents an economy in power, but also leads to the production of smoother deposits. In this respect the fluoride solution as above prepared is slightly inferior to the chloride as shown by the data in Table VII based on approximate measurements at 25° C. (77° F.)

Efforts were therefore made to increase the conductivity by the addition of sodium sulphate and magnesium sulphate re-

spectively. It is interesting to note (Table VII) that the sodium sulphate has a greater effect upon the conductivity than has an equivalent amount of magnesium sulphate, though the change produced by this concentration of either is not sufficient to represent any great economic advantage. Unfortunately, there is no prospect for the development of a good nickel-depositing solution with a resistivity comparable with that of the acid copper bath (about 5 ohms per cm. cube).

A few experiments with solutions corresponding to Nos. 4 and 5 in Table VII showed that good deposits could be secured in them within about the same range of current density, as in No. 3. No physical tests were made upon the deposits, but from simple bending tests they appeared to be somewhat "softer" than the deposits from No. 3. At the same time it was found that there was slightly less tendency for the deposits from Nos. 4 and 5 to crack and curl up than for the deposits from No. 3. The advantages observed were not sufficient, however, to justify a definite recommendation to add these "conducting salts" to the solution.

One of the chief objections to the use of solutions prepared like No. 3 is the danger and inconvenience of handling hydrofluoric acid. In our later experiments, therefore, a bath was prepared according to the formula of No. 6 (Table VII). The substitution in No. 3 of sodium fluoride for nickel fluoride, with the addition of an equivalent amount of nickel sulphate, should produce a solution exactly similar to that which would be secured by adding 0.2*N* sodium sulphate to No. 3. The value for the conductivity of such a solution and its behavior upon electrolysis indicates that such is the case. This bath has not been used by us on a commercial scale for so long a period as has No. 3, but the results thus far obtained are sufficiently promising to recommend its further application. Apparently, the deposits are slightly softer than those from No. 3, which may cause somewhat less resistance to abrasion. On the other hand, such deposits may be preferable in electroplating because they are more readily buffed. A bath of this character has been used by us for miscellaneous plating for a few months, and has given entirely satisfactory results.

VI. CONCLUSIONS.

1. When nickel or sodium fluoride is added to nickel baths containing boric acid, fluoborates more complex than those corresponding to the formula HBF_4 are probably produced.

2. The fluorine content of such solutions can be determined approximately by titration with ferric chloride.

3. The hydrogen ion concentration of nickel solutions can be determined approximately by suitable indicators. Results with the hydrogen electrode are apparently less reliable.

4. The effect of boric acid and hydrofluoric acid upon the hydrogen ion concentration and neutralization curve of nickel sulphate solutions has been studied, and their function in plating solutions has been suggested.

5. Nickel deposits produced in solutions containing fluorides have a finer structure and a higher tensile strength than those produced in corresponding chloride solutions. When prepared with anodes containing about 97 percent of nickel, there is slightly more iron and copper in the fluoride deposits than in the chloride.

6. The anode corrosion in solutions containing fluorides is good and the solutions produce less sludge than do corresponding chloride solutions. Attempts to use electrolytic anodes in such solutions at reasonably high current densities have not yet been successful, but the results with hot rolled anodes are promising.

7. The use of fluorides in nickel solutions for electrotyping will probably increase the wearing quality of the printing surface. In electroplating, good deposits can be secured in the presence of fluorides at somewhat higher current densities than are ordinarily employed, and these deposits, while slightly harder to buff, show greater resistance to abrasion.

8. The use of the following solutions is suggested:

Solution "A."

		g/L	Oz./gal.
Nickel sulphate	1.8 *N*	255	34
Nickel carbonate*		12	1.6
Hydrofluoric acid* (50 percent)		8	1.1
Boric acid	0.5 *M*	31	4.2

* Equivalent to 0.2*N* nickel fluoride.

This solution is prepared by adding the hydrofluoric acid cautiously to the nickel carbonate which has been previously mixed with water to the consistency of a thick cream. After effervescence ceases, the boric acid, first dissolved in warm water, is added, and the entire mixture is then added to the solution of the nickel sulphate. After thorough mixing the solution is filtered or allowed to settle.

Solution "B."

		g/L	Oz./gal.
Nickel sulphate	2.0 *N*	281	37.5
Sodium fluoride	0.2 *N*	8.4	1.1
Boric acid	0.5 *M*	31	4.2

This solution is prepared simply by dissolving the three constituents in water. By using warm water, solution occurs more rapidly.

These solutions may be used with an average current density of from 3 to 4 amp./dm^2 (28 to 37 amp./sq. ft.) for producing adherent deposits in electroplating, and 1.5 to 2 amp./dm^2 (14 to 19 amp./sq. ft.) for making reproductions, as in electrotyping.

The author desires to express his appreciation for the assistance of his associates at the Bureau of Standards, especially W. E. Bailey, L. D. Hammond, H. E. Haring and M. R. Thompson, in conducting the experiments described in this paper.

DISCUSSION.

Wm. Blum: In considering this paper and that of Mr. Madsen, it is necessary to take into account the fact that we were working on nickel deposition with two diametrically opposite purposes; Mr. Madsen wanted to get his nickel as soft and ductile as he could, and we wanted to get our nickel as hard as possible. Any apparent contradictions are therefore justified. I think we can say with fairness to both papers, certainly to my own, that the

results are only suggestive and indicate principally the need for exhaustive studies on nickel deposition. The fact that great differences can be secured by apparently trivial changes in the procedure shows that we do not know the underlying principles very well.

The actual determination of the hardness of thin sheets is far from a satisfactory measurement. Since publishing this paper, we made a few approximate measurements of Brinell hardness, and found that the "chloride" deposit has a hardness of 130 and the "fluoride" of about 200, showing that the hardness is roughly proportional to the ultimate tensile strength.

R. J. McKay[1]: I would like to state that Dr. Blum's paper is one of the few papers that we have heard on nickel deposition, in which the author does not attempt to make sweeping generalizations regarding conditions which he does not control. For instance, he realized that these things are interdependent, that the effect of hydrogen-ion concentration depends also on other characteristics of the solution, and I hope very much that Dr. Blum will be able to complete his experiments in the same open-minded manner that he has begun them. I think that we will learn a great many interesting things about nickel deposition in this way. I would like to know the value of the pH of a pure boric acid solution compared with the value of the equivalent fluoboric acid mixture.

Wm. Blum: These figures are only approximate. A saturated solution of boric acid has a pH of about four. If hydrofluoric acid is added to the boric acid, we get an acid which is stronger, *i. e.*, has a higher degree of acidity (a lower pH) than either hydrofluoric or boric acid alone.

I wish to emphasize a point, which is fundamental to the investigation of any solution for electro-deposition; if you cannot analyze the solutions at the end of a certain period of operation, the results are, at least, of only qualitative significance. We may be perfectly justified, from the standpoint of expediency, in operating solutions we cannot analyze, but at any rate let us recognize that our conclusions based upon them must be tentative. I

[1] Mellon Institute, Ind. Res., Pittsburgh, Pa.

would suggest to our educational institutions the problem of the determination of fluorine in the presence of boric acid, especially where a large amount of sulphate is present.

In the paper we stated that we had finally secured a method for the determination of fluorine which we believed was satisfactory, *i. e.*, titration with ferric chloride. Subsequent work has shown that this method is subject to error in the presence of boric acid. More recently we have attempted to apply the method depending upon the precipitation of lead-chloro-fluoride, and have obtained promising results.

(*Communicated*): Experiments conducted since then, at the Bureau of Standards by Dr. L. D. Hammond have shown that the lead-chloro-fluoride method yields reliable values, and this method is now being used by us for control work.

H. S. LUKENS[2]: I would like to ask one or two questions about the handling of the hydrofluoric solution. Is it particularly hard to handle, and how would it act on wood or lead lined tanks? I would also like to ask whether any of Dr. Blum's experiments were carried out in such a manner that he could make any statements about the power used per pound of nickel produced.

WM. BLUM: Hydrofluoric acid can be handled on a small scale in lead-lined tanks or in wooden pails. For the safety of the workman, it is better to get away from the use of hydrofluoric acid, and we therefore recommend the use of solutions containing sodium fluoride, which is safe to handle.

As far as power is concerned, we get a very high current efficiency in these solutions, but, on the other hand, the resistance of the solution is possibly a little greater than that of the ordinary chloride solution. We did not make accurate measurements of polarization, but that is probably at least as great in the fluoride as in the chloride; so that the power consumption may be slightly greater than that used in ordinary nickel refining.

[2] Asst. Prof. of Chemistry, University of Pennsylvania, Philadelphia, Pa.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

DUCTILE ELECTROLYTIC NICKEL.[1]

By Chas. P. Madsen.[2]

Abstract.

Records the discovery by the author that if cathodes in a nickel electrolytic bath are periodically lifted out of the bath, exposed to the air, and reimmersed within a certain limiting time, the nickel deposit does not laminate but is greatly improved as regards freedom from pitting and mechanical properties. Automatic apparatus for lifting out the cathodes at proper intervals and keeping them out the proper time, was devised, resulting in nickel of greater ductility and tensile strength than heretofore obtained. The deposit has great malleability and surprising hardness, by Brinell test, considering its high ductility. [J. W. R.]

The general failure to produce alloys for electrical heating purposes by metallurgical means, which would come outside of the patent situation which developed in 1916,[3] led to the conception that a better type of resistance alloys and armors for heating units could be made by electrodeposition. It was believed that nickel or cobalt would be the best major ingredient and it was taken for granted that disclosed processes for making heavy deposits of these metals produced the results claimed. A few trials, however, soon showed this belief concerning nickel to be an error. In some cases claimed results of the inventor could not be reproduced while in others a heavy deposit could be obtained only once in the same electrolyte, and in all cases the metal produced was mechanically very imperfect and became even more brittle after heating.

[1] Manuscript received March 12, 1921.
[2] Electrochemical Engineer, New York City.
[3] Marsh patent No. 811,859.

Attention was then turned to cobalt, and better results were obtained but not perfect enough to warrant the added cost. A more thorough review of the nickel art was then made and research instituted for determining the factors governing the production of heavy and mechanically perfect deposits of nickel.

All known baths were tried and particularly was Dr. O. P. Watts' review[4] followed carefully. The work has occupied a period of over five years, during which time several thousand deposits of 1/32 inch. (0.8 mm.) thick and over have been made, It has, however, been carried out largely by empirical methods, and sufficient data have not yet been obtained for formulating the physical factors on a scientific basis. However practical results have been produced, which appear worth while recording at this time.

This paper is therefore intended only as a report of the general work done and how the result was obtained, and it is hoped that the physical data can be standardized at an early date and be made the subject matter of a subsequent paper.

The early work was concentrated upon the electrolyte, and the results were so erratic and inconstant that the following general conclusions were drawn:

First: The usefulness of any nickel electrolyte can be determined only after its entire metal content has been replaced from the anode.

Second: No conclusion can be drawn from deposits less than 0.01 inch (0.25 mm.) thick.

Third: Reports of results with any electrolyte are of no value, without knowing the exact analysis of the anode used.

It was found that no electrolyte would entirely fulfil the first condition with any type of commercial anode, and the results were therefore variable. The so-called 97-98 percent cast anodes containing manganese were found to deteriorate the bath most rapidly, while anodes of the same nickel percentage containing tin performed little better and introduced the difficulty of forming metastannic acid under certain conditions. On the other hand, it was found that while the so-called 92-96 percent cast anodes containing iron maintained the bath nearly constant, although

[4] Trans. Am. Electrochem. Soc. (1913), 23, 99.

their efficiency was rarely 100 percent on their nickel content, the large amount of ferric hydrate caused considerable difficulty in making heavy deposits. It was also found that the ratio of the anode to cathode surface was more important than usually supposed and was apparently a function of the anode composition. It was in all cases necessary to have from two to five times greater anode surface than that of cathode, and in some cases from ten to fifteen times.

Attention was then turned to the use of relatively pure nickel metal as anodes. Some investigators state that pure nickel is passive while others claim good results with its use as anodes. Imported pure nickel made by Fleitman[5] and Pfanstiehl were tried, also hot rolled nickel and electrolytic nickel made by the International Nickel Company, as well as domestic so-called cold-rolled malleable nickel. In these cases it was found necessary to have some chloride present, but a limit was found beyond which any further chloride addition did not improve the result in each case. The imported pure nickels performed fairly well for a time but became passive in a variable and most exasperating manner without apparent cause. The hot-rolled material was always more passive in the same electrolyte than either of the imported pure nickels, or any of the cast anodes, and also varied in its performance. Hammond[6] and Mathers[7] report the successful use of International electro-nickel as anodes, particularly after annealing, but the annealing methods are not described. It was found that such material unannealed was even more passive than either the imported pure nickel or hot-rolled; annealing always improved their action, but different methods produced different results. Electro-nickel annealed in an atmosphere of CO dissolved with an efficiency of about 95 percent and did not turn passive as readily as either pure material, but sufficiently so as to cause pitting. Their use for heavy work was, however, furthermore rendered impractical, because of the fact that they dissolved irregularly producing a sort of lace structure which readily crumbled, causing thereby a loss of from ¼ to ½ of the anode and making the cathode deposit very rough unless the

[5] Vereinigte Deutsche Nickel Werke. Chem. News, 1879, Vol. 40, p. 67.
[6] Trans. Amer. Electrochem. Soc. (1916), **30**, 103.
[7] Trans. Amer. Electrochem. Soc. (1916), **29**, 383.

anodes were held in bags. The domestic so-called cold-rolled malleable nickel performed the best of any nickel tried, particularly with the proper amount of chloride present in the bath. They dissolved with an efficiency of about 97 percent when free from passive portions. This type of anode was therefore used exclusively in the subsequent three years of this investigation. The average analysis of this material is as follows:

Ni	95.30
Fe	2.13
Cu	0.25
Mn	0.33
C	0.30
Si	0.23

Dr. Langbein[8] and others report the use of rolled anodes extensively in Europe, and state that their alkali and acid-forming characteristic is the reverse of that of cast anodes. It is not clear why this should be so, and the statement has been questioned. It was, however, carefully checked and found to be correct, and furthermore the ratio at which a neutrality balance is maintained was found to be very exact. It was found that when the anode is 1.77 times the area of the cathode, the bath will remain relatively neutral for long periods of time. Any increase of anode surface over this turns the bath acid and any decrease turns it alkaline, provided, however, the anode is free from passive portions. Unfortunately, however, such portions were often present, in which case the bath would always turn acid. Sodium sulphonate alizarin was used as an indicator for this purpose. Using these anodes, the general conclusions on electrolytes were as follows:

Nickel-ammonium sulphate is never an advantage over nickel sulphate as a metal carrier. A little alkali metal salt, however, should be present. The addition of conductive salt, as magnesium sulphate, etc., permits of a higher current rate, but the baths are not stable and reliable. The addition of citrates and other organic compounds diminishes the amount of sludge and favors the production of smooth and bright metal, but such baths are exceedingly unstable and the metal produced is always more brittle and cannot be carried to the same thickness as in the same electrolyte without the addition agent.

[8] "Electro-deposition of Metals," 7th Ed., p. 273.

It has been reported by others that while a nickel electrolyte should be nearly neutral some free hydrogen ions are necessary. This was found to be correct and that boric acid is the best carrier of such hydrogen ions. It is necessary to have some chloride present, but a bath consisting of nickel chloride only would not produce perfect metal even when containing boric acid. It was found that nickel chloride was best and Dr. Watts'[9] bath was finally adopted as standard for most tests. This bath has, however, recently been modified and addition agents introduced.

Warming the electrolyte is an advantage in all cases, but usually little improvement was obtained above 55° C.

With this modified bath, using the cold-rolled nickel anodes described, many deposits, upwards of 1/16 inch (1.6 mm.) could be made in succession, but they were not fully malleable, nor would they stand heating without becoming more brittle, and they often contained pits and other mechanical imperfections.

Other investigators have shown that the embrittlement of electrolytic nickel and perhaps pits are caused by hydrogen. Various means were tried for eliminating hydrogen. It was found that agitating either mechanically or by air resulted in no benefit, but often instead resulted in a much rougher deposit. Various manipulations of the cathode, as shaking and striking, were tried, but without benefit, and it was observed that the hydrogen bubbles would immediately return after removal. Brushing the cathode mechanically was tried, and it was found that while the deposits thus produced possessed a mirror-like smoothness, they were even harder and more brittle than those produced without brushing.

Since one object of this work was the production of armors for electrical heating units, the deposits were made on objects which were supposed to simulate the character of surface which such a heating unit would possess for coating. These objects were glass tubes about ⅜ in. (9.5 mm.) in diameter and 3 in. (7.5 cm.) long. They were prepared for deposition by the well-known silver-fire process. Several hundreds of these were made and one reason for adhering to their use was the observation that in

[9] Trans. Amer. Electrochem. Soc. (1916), 29, 395.

addition to determining the limits of the thickness by the deposit bursting open, it would often happen that a deposit would build up thick and develop sufficient strain to crush the glass. In this way data could be obtained on those deposits which did not peel nor crack open.

The use of these glass tubes as cathodes, however, led to a discovery in a peculiar way. If the deposit cracked open it would nearly always do so along the bottom, and would often occur a considerable time before being observed. In the anxiety to save time and to detect the crack as soon as formed, the cathodes were often jerked out of the bath quickly in order to inspect the bottom of the tube for cracks and then reimmersed. Since it is taught in the art that interruption of current or removal of the cathode will result in laminated deposits, a careful record of these removals was kept and when a large number of cathodes were studied the surprising fact was disclosed that all those which had been subjected to this removal for observation were both much thicker and much more malleable than others, almost regardless of other conditions. A cathode was then made which was removed and re-inserted quickly every few minutes for twenty-four hours. This was found to be by far the most perfect deposit produced.

The time factors were then determined for both the period of exposure and the period of deposition. It was found that, contrary to former beliefs, the cathode removal, if not over 15 seconds in duration, produced no laminated deposits, but instead, homogeneous and highly ductile deposits. It was also found that the frequency of removal necessary for producing the best result depended upon the factors of deposition influencing the formation of hydrogen, such as anode efficiency, temperature, acidity and current density. With the improved bath mentioned above, operating at 55° C, with a current density of 72 amperes per square foot (8 A. per sq. dm.), it was found that with 97 percent commercial cast anodes, this necessary frequency of removal or deposition period was 30 seconds to one minute, while with the cold-rolled anodes it was about one to five minutes. An automatic device was then constructed for carrying out this operation, and all of the sample deposits made at the Bureau of Standards

and which were exhibited at our last Atlantic City meeting were made by this means.

A physical study of the metal so produced showed that it possessed a far higher degree of ductility than was expected, even exceeding that of any nickel heretofore produced. It was found to have a slightly lower electrical resistivity but a slightly higher density. It was, furthermore, found that the deposited metal could be heated red-hot either before or after rolling without embrittling it. Wires have been drawn from a bar ⅛ inch (3 mm.) in diameter down to 0.002 inch (0.05 mm.) without annealing. This new nickel however develops considerable hardness and increase in tensile strength upon rolling or drawing. The tensile strength of the deposited metal is about 72,000 pounds per square inch (50 kg. per sq. mm.) while the wire mentioned above showed a strength of 250,000 pounds per square inch (175 kg. per sq. mm.). The Brinell test of the deposited metal is about 130, while that of metal which has been rolled from a plate ⅛ inch (3 mm.) thick to 1/32 inch (0.75 mm.) is about 150 Brinell, and it is still malleable. Tests with the Ericsson machine showed a drawing ability better than that of ordinary hard-rolled brass or copper and about equal to dead soft copper.

The average analysis of this new electrolytic nickel is:

Ni	99.70
Fe	0.01
Cu	nil
C	0.02

A contemplation of the general utility of a metal of such remarkable properties in the face of certain war demands, caused relegation into the background of the original object of producing electric heating or resistance units, and we concentrated instead upon the development of production of sheet metal and of various intricate forms as dies, moulds, etc., for industrial purposes. It was soon found, however, that while the metal produced by the means outlined above was highly ductile, it was not always mechanically perfect. The principal trouble was pits of various types, which would appear and disappear in the most exasperating and unaccountable manner. Much has been written concerning

the nature and cause of pits in nickel plating, but without any permanent remedy having been found. The last two years of this work were therefore devoted, more or less, to an investigation into the cause and remedy of pits. Many old means were tried for their elimination but without good results.

It was found that small solid particles would cause imperfections, but that the type of pits most troublesome was not so caused. It was also found that excess of air in the electrolyte, which has been shown to be a cause of producing pits in the electrodeposition of lead[10] was not a primary cause, although its presence might exaggerate the pits if the primary cause were present. The influence of the exact degree of neutrality with relation to solvent acid hydrogen ions was also studied, and it was found that while more hydrogen was generated and a less malleable metal made in an acid bath, that this condition is not the primary cause of pits, but will only exaggerate them, if the primary cause is present. The primary cause of pits was finally traced to inherent characteristics of the anode.

The metallurgy and refining of nickel was then studied and several hundred different kinds of anode castings made. A new anode composition was finally found which, when used with the hydrogen elimination process produces pitless metal continuously and without diminishing the metal concentration of the bath. It was furthermore found that for reasons which are not altogether clear this anode causes the generation of so small an amount of hydrogen that the necessary frequency of cathode removal is decreased from every five minutes to every two hours.

Many castings have been made which require a removal only every ten or fifteen minutes and will make pitless metal up to 1/32 inch (0.75 mm.) thick, while a few casts have been made which require removal only every two hours and pitless cathodes have been made with these up to ⅛ inch (3 mm.) thick. Indications are that the perfection of these anodes will enable the production of pitless metal of any thickness even without the hydrogen elimination process.

It is thought best to defer the disclosure of this anode until it is fully developed and standardized on a commercial basis.

[10] Trans. Amer. Electrochem. Soc. (1919), 35, 279.

DISCUSSION.

J. F. THOMPSON[1]: If I might take a moment, I would like to call attention to an apparent error in Mr. Madsen's paper. On page 485, he discusses the use of rolled malleable nickel anodes, but on page 486 quotes an analysis which is apparently an analysis of commercial cast anode, and not of malleable nickel. I think he will probably want to correct that.

Mr. Madsen has headed his paper "Ductile Electrolytic Nickel." All electrolytic nickel as produced by the refineries is ductile. The essential point of Mr. Madsen's work is that he produces a nickel of good mechanical properties, free from holes and laminations.

COLIN G. FINK[2]: Does not Mr. Madsen try to emphasize that he can obtain ductile deposits an eighth of an inch thick which are still malleable and soft as compared to present practice?

J. F. THOMPSON: Ordinary electrolytic nickel is sold in the market today three-eighths of an inch thick and can be rolled down to 0.005 without annealing, and very pure samples of nickel wire are made by cutting cathodes into strips and drawing them down to fine wire without annealing.

A MEMBER: I would like to ask those who have been working on this problem, whether anyone has made any effort to determine the hydrogen content of deposited nickel to determine whether the hardness is related to the hydrogen which apparently exists in electrolytic nickel?

WM. BLUM[3]: We have made no actual determination of the hydrogen content of the nickel, but there seems to be no reason to doubt that the brittleness of nickel which is deposited at an excessively high current density or in an excessively acid solution, is connected with the evolution and adsorption of hydrogen. For purposes of wear and abrasion, the nickel should be hard, not because of its gas content, but because of some permanent physical characteristics.

I would like to call attention to a point mentioned in both Mr.

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[2] Consulting Electrometallurgist, So. Yonkers, N. Y.
[3] Chemist, Bureau of Standards, Washington, D. C.

Madsen's paper and my own, and that is the question of anode corrosion. I believe that it is highly important to be able to get solutions and conditions of operation which will permit the use of high purity nickel anodes, instead of using nickel anodes such as are now mostly used and in which impurities are intentionally added. The manufacturer of anodes buys pure nickel and adds iron and carbon and tin, etc., in order to enable him to cast it and to increase the anode corrosion. We should certainly try to overcome that condition. There is a statement on page 486, Mr. Madsen's paper, to the effect that when the anode is 1.77 times the area of the cathode, the bath will remain relatively neutral for long periods of time. That is perhaps too dogmatic, unless the current density is specified. In a given solution the anode current density will determine anode efficiency, and for this reason such a statement can only be true at or about a certain current density.

J. F. Thompson: We made some rough determinations of the hydrogen content of our electrolytic cathode. They were rough, unquestionably, but were done on a number of pieces and showed a considerable volume of hydrogen in the normal cathode. In regard to Mr. Blum's statement on malleable anodes having a purity of 98.75 nickel plus cobalt—they are commonly used abroad and in the Orient, and certain people are using electrolytic nickel of 99.75 to 99.80 nickel plus cobalt, commercially, and claim they are corroding perfectly well.

C. J. Rodman[4]: I would like to ask how the hydrogen content of this nickel was determined, and also I would like to ask Dr. Blum if he has tried vacuum annealing of his nickel, and the effect of that on its properties, its hardness, etc.

J. F. Thompson: I can answer the first question by saying that I do not know how that was determined. The result came up some years ago from the research department, and I do not now recollect how it was determined.

Wm Blum: As indicated in the paper, we have made no extensive study of the effect of heat upon the physical characteristics of

[4] Research Chemist, Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.

this metal because we knew that any heating would make it softer and we wanted to make it as hard as we could. Unquestionably the crystal characteristics and the gas content will be materially changed by heating.

J. F. THOMPSON: I wonder if that hydrogen content had any effect on the hardness?

WM. BLUM: It must have had, but it would be difficult to expel the hydrogen without making other changes.

J. W. RICHARDS[5]: Mr. Madsen certainly believes that he has made a nickel more malleable and more ductile than any deposited nickel that has been made before. On page 489 he states that "wires have been drawn from a bar ⅛ inch (3 mm.) in diameter down to 0.002 inch (0.05 mm.) without annealing," which has not been done before with nickel. Concerning the periodic lifting of the cathode out of the bath, and the reason why this improved the quality of the nickel, Mr. Madsen's idea was that it was connected with the adsorption of hydrogen by the deposited metal; he evidently thought that hydrogen bubbles forming on the cathode were not adsorbed until they reached a certain size, and by lifting the cathode out periodically, these little globules were allowed to burst and thus removed themselves before they obtained this critical size. I differed with him on that explanation; I thought it was more likely—and this I would offer as my explanation—that the lifting of the cathode out brought the layer of electrolyte which wetted the cathode in contact with the air and gave it some oxygen content, that when this oxygenated film of electrolyte was returned to the bath, then for a certain time it took care of the hydrogen which was coming along, or de-polarized it, if one likes to say that, so as to suppress the adsorption of the hydrogen by the metal. That seemed to me a rational explanation of the suppression of the hydrogen, and the changing or improving in quality of the metal.

E. O. BENJAMIN[6]: The nature of the electrolyte at the top surface of any bath is invariably of a different constitution than the lower portion, as is readily noticed by the rapid corrosion of the

[5] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.
[6] Consulting Engineer and Chemist, Newark, N. J.

anode on the top surface, and the deposit of a cathode which is submerged, part of which protrudes above the electrolyte at the top surface, invariably has a softer nickel deposit, although the rate of the deposition is very much slower. I might bring out another fact, that in some experiments made in plating or depositing nickel on a machined cast iron surface without any particular care in purifying or cleaning the surface any more than just a straight pickling so as to permit the stripping of the nickel from that surface, we found a small amount of cast iron adhering to the nickel that had been on the surface of that iron. In pickling this off in any of the acid pickles, we found that a sheet of 0.005 to 0.010 of an inch thick was very brittle. In folding over, it invariably cracked. On boiling this in hot water for a period of anywhere from three to four days the material permitted bending over and back again on itself, with a slight hammering, before it broke, so that this apparently shows that the hydrogen plays an important part in hardness and ductility because the pickling process invariably causes a hydrogen adsorption.

H. S. Lukens[7]: It would be very interesting to know what the hydrogen ion concentrations are which Mr. Madsen uses in his process. He states that his solutions are nearly neutral, but gives no relations of the hydrogen ion concentrations.

Wm. Blum: He does state in the paper that they were nearly neutral; the chloride solutions do tend to become somewhat more nearly neutral than the fluoride solutions, so I would judge that he was working with a pH about 5.5 to 6, although I have not any actual measurements on it.

J. W. Richards: Mr. Hogaboom, were he here, would undoubtedly say that the trouble with new electroplating processes is that they start with a well-known, well-defined bath, and anodes and cathodes, but the question is, are they going to be able to run that for a week or a month or six months and get the same results? Now undoubtedly the electroplaters have to improve their art in the same way that the electro-refiners have, by having absolute control over the composition by proper analyses, and in the case of nickel, particularly, by having control of

[7] Asst. Prof. of Chemistry, University of Pennsylvania, Philadelphia, Pa.

the anode corrosion, so that the anode feeds the bath. Mr. Madsen gave me the impression in our conversations that about one-half of his problem was concerned with the corrosion of the anode and keeping the bath fed with nickel; that was the reason he put so much emphasis on it in his paper.

A MEMBER: In connection with this depolarization action to which Professor Richards has referred, as an explanation, I wonder if nitrates or any similar depolarizers have produced noticeable effects? What would be the effect of a little nitrate or other not too easily reduced anion?

J. W. RICHARDS: I think the point involved is that if you put a nitrate in the bath, you will have it distributed throughout the whole bath. You want it to act right at the surface of contact of the electrolyte with the nickel, and by lifting the plate out you get the film of electrolyte oxidized just where you want it, and I think that perhaps would be a second reason for preferring this method of depolarizing to the other.

R. J. MCKAY[8]: May I add to that, that the experiments that the International Nickel Company have made show that in general it is not practical to depolarize with strong oxidizing agents. Nitrates particularly are almost always detrimental to nickel deposits.

W. E. HUGHES[9] (*Communicated*): A principal merit of Mr. Madsen's paper is the attention he devotes to the anode side of the nickel-plating tank. The composition and physical condition of the nickel anode are matters that have been far too little attended to. This is, no doubt, in part due to the indifference of manufacturers and in part the result of neglect (probably the result of want of knowledge) by users in works practice. Mr. Madsen's work should show to the latter that "any sort of anode" will not do; it is both wasteful and expensive, leading, as its use may easily do, to bad work and expensive operation. If users wake up to the fact that the use of an anode of a certain composition and physical state will result in better and cheaper work then manufacturers will have to supply such anodes. This will entail

[8] Industrial Research, Mellon Institute, Pittsburgh, Pa.
[9] Elec. Met., 6 Coleherne Terrace, Earls Court, London, S. W. 5, Eng.

greater care in manufacture; and the matters that will have to be considered have been clearly indicated by Mr. Madsen. A point mentioned by him in regard to the anode made of electrolytic nickel struck me as of much importance. He says that such an anode dissolves better after annealing. If one thought about it, one might expect that that would be so; but Mr. Madsen has the merit of bringing out that point in his paper. It is related to the problem as to what should be the physical condition of a first-class nickel anode, and this is, of course, a matter of metallurgical treatment-casting temperature, rate of cooling, and so on. It would be of interest to know whether Mr. Madsen considers that the anode of his choice would behave equally as well in other baths as in the modified Watts' solution he employed.

There is one remark made by Mr. Madsen on which I join issue with him, and that is the one referring to the use of magnesium salts in nickel baths. He says that solutions containing such salts are "unstable and unreliable"; but he does not give his grounds for that view. My own opinion, based upon long works experience, is, that a solution made of nickel sulphate and magnesium sulphate as the principal constituents is hard to beat as a bath of general utility; and I should very much like to know what Mr. Madsen means by the word "unstable," as used by him in reference to magnesium-containing nickel baths.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

A NEW HIGH CAPACITY STORAGE BATTERY.[1]

By C. W. Hazelett.[2]

Abstract.

Description of a very thin plate storage battery, having about three times the exposed surface per pound of material compared with any other commercial battery. The electrical output per unit weight of lead and active material is 50 to 200 percent higher than that of the standard types, and it is less subject to mechanical defects and variability. Batteries may be re-built by shipping charged elements wrapped in paper, the separators between the plates not allowing them to dry out in transit.—[J. W. R.]

It has been common knowledge for some time that the capacity of a storage battery of the lead acid type is principally a matter of surface. It has also been shown that the plates of the lead acid battery known as the Ironclad and of the Edison alkaline cell, in which the active materials are so held mechanically that erosion is retarded, give extraordinarily long life when compared with batteries not having this feature. It has been proven that at commercial rates of discharge in batteries of the lead acid type the active portion of the positive plate is not over 1/32 inch in depth, the material at a greater depth in the plate being simply reserve to give added life to the plate after the surface is washed off.

Furthermore, the tendency in the construction of vehicle type batteries has been to decrease the thickness of the plates to the greatest possible extent primarily to decrease their weight. This is limited by inability to cast grids of commercial dimensions below approximately ⅛ inch in thickness. The thinnest plates used commercially today considering both positives and negatives, average about this thickness, whereas a few years ago it was customary

[1] Manuscript received February 12, 1921.
[2] Storage Battery Engineer, Cleveland, Ohio.

to use positives having 3/16 to 7/32 inch (5 to 6 mm.) or even ¼ inch (6.5 mm.) thickness.

It is believed by many battery men that a thin plate battery is necessarily a short-lived battery. It is true that for a given number of plates having a certain area and using standard construction decreasing their thickness decreases their life in service. However, for a given amount of material or, in other words, for a given weight cell, the total life is considerably increased by decreasing the thickness and using a larger number of plates to bring the cell to the same weight. This is true for the following reasons: For a given charging or discharging rate, the ampere density per unit area is considerably less. This decreases the rate of sulphatization per unit area on discharge and the amount of heating for a given current rate of charge. Heating of a cell is responsible for a softening of the active material in the positive, buckling of plates and rapid deterioration of separators. A cell with a large number of plates naturally has lower internal resistance and the heating is very much decreased. Furthermore, the amount of gas given off per square inch or per plate with a given rate of charging is less, decreasing the mechanical erosion of the plate due to bubbles of gas. Since a battery having a large capacity requires charging less frequently in a given service and since most of the destructive heating and gassing takes place at the end of charge, fewer charges means longer life of the battery. Since more surface is available and the active material more accessible, a cell with a large number of very thin plates will be charged almost fully before it begins to gas, further reducing the above mentioned deleterious charging effect.

It is customary to use a perforated rubber separator in contact with the positive plate of vehicle batteries to assist in holding the active material in place. This is rather expensive but has resulted in a very large increase in life. However, it is true that after the immediate surface in contact with this separator has been washed off and the surface material escaped thru the pores of the separator, the life of the core is very short. We might well adopt the slogan "Save the Surface and you Save all".

With these principles in mind, The Hazelett Storage Battery Co., of Cleveland, has developed a battery having approximately 3

times the amount of surface exposed per pound of material compared with any other commercial battery, and so constructed as to hold the active material in place by inexpensive means.

A grid is used which is approximately 1/32 inch (0.8 mm.) in thickness. As it is not practical to cast a grid of this thickness, continuous sheets of cast lead alloy of the proper thickness are manufactured on a special machine developed for the purpose, and subsequently the grids are punched from this sheet. The grids are then pasted with active material, and the positive and negative plates stacked alternately using a plain flat piece of special wood fibre as a separator between the plates of opposite polarity, which entirely fills the space between the plates. These separators extend considerably beyond the plates at all sides to prevent short circuits. The element then, thus built up, without clearance of any kind between the plates and having the space between the active portions of the plate entirely filled with this porous separator, is set in a burning rack and the projecting lugs of the plates welded together to form the terminals.

A complete element is shown in Figure 1. It is obvious that an exceedingly large surface of material is exposed to the electrolyte and that since the element is assembled as a snug fit in its container, it would be impossible for active material to escape from the plates. The following questions are usually asked by storage battery men concerning this battery:

1. Is it not necessary to have grooves in the separators next to the positive in order to get circulation?

2. How can the gas escape without channels provided for that purpose?

3. Will the battery give capacity at high rates of discharge?

4. Will not the separators clog and cause the battery to lose capacity?

5. Can sufficient electrolyte be held in the separators to supply a complete discharge?

6. Do the plates buckle?

Answer 1: Grooves in separators next to the positives do increase the positive capacity appreciably. However, the increase in capacity due to the amount of surface present is so far above the decrease due to the absence of grooves that a very large increase

in capacity remains. Furthermore, when the thickness of both positive and negative plates is decreased, it is found that the capacity of the negative plates per plate decreases more rapidly than that of the positive and the limiting factor is not the capacity of the positive plate at all. If insufficient circulation occurred, one of two things would be expected; first that the capacity on discharge would be low and second that the cell could not be charged rapidly. These conditions do not exist and as tests show a liquid will diffuse through the separators in six seconds it would

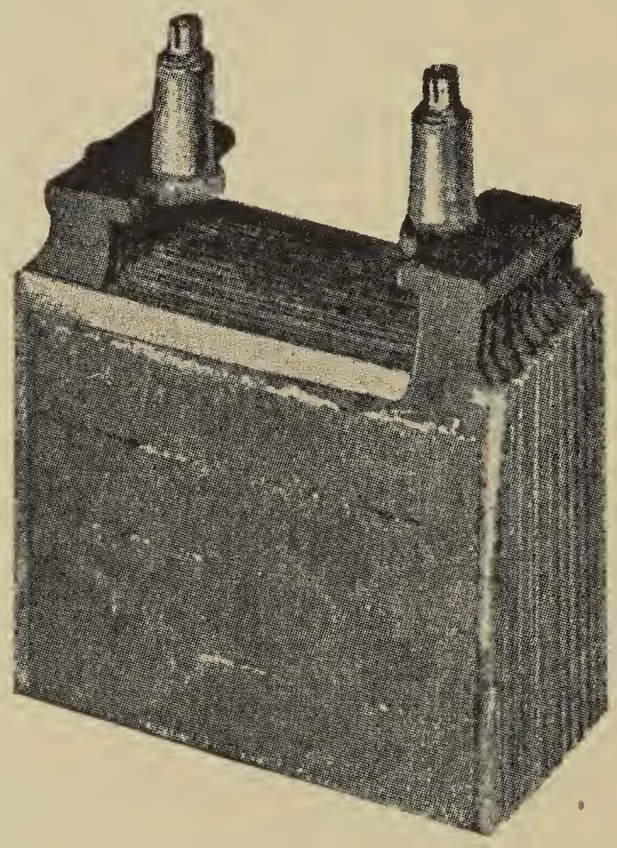


Fig. 1.

not be expected that any appreciable decrease in capacity would occur from this cause. However, the vertical circulation in the cell is slightly impaired so that at high rates of charge or discharge a hydrometer does not give accurate indication of the amount of energy still available in the cell without allowing some time for equilibrium to obtain. This is true of all cells to a certain degree, however, and there is no great disadvantage from a practical standpoint.

Answer 2: In practically all commercial storage batteries of the portable type, the plain ungrooved side of the separator is in contact with the negative plate. When a cell gasses, two volumes of

hydrogen are given off at the negative to one volume of oxygen from the positive and excepting a little more polarization at the negative, no unusual conditions have been experienced incident to the escape of gas. Since the sides of our separator next to the positive are also flat, no difficulty would be expected and there is none. The fact remains that the gases escape without appreciable detriment to the plates.

Answer 3: The capacity performance of this battery improves in comparison with other batteries as the conditions requiring rapid circulation become more serious, as at high rates of discharge or at low temperature. The following relations approximate the performance attained compared with the highest capacity battery now in commercial use. At the 6-hour rate of discharge, the watt hour performance is approximately 50 percent higher and at the 20 minute rate of discharge it is roughly 100 percent higher per unit weight of battery.

Answer 4: The separator is held in direct contact with the surface and completely fills the space between the plates, and the material does not lose contact with the plate so as to sulphate. The writer has never experienced any tendency to clog due to the active material. Life tests giving double the total ampere hours per pound obtained from standard cells showed no difficulties whatsoever from this cause. The material finally becomes exceedingly soft and black in the positives but does not escape appreciably from the plates. The voltage of the cell on discharge is very high, while the ampere hour capacity drops off slightly. The separators seem to give extraordinarily long life on account of the low temperature conditions under which they work, and because there is no vibration of the element, it is practically unnecessary for the separator to have any mechanical strength whatever. The separators are mechanically almost perfect and no cases of re-insulation have ever been necessary.

Answer 5: It is surprising to even most storage battery men that the woods which are used commercially for storage battery separators have a void space of from 65 to 85 percent of their total volume. Fortunately this relation works out so that a separator having proper mechanical characteristics holds suitable quantities of electrolyte for the operation of this cell.

Answer 6: The plates are so thin that if one is allowed to buckle a light pressure of the finger will straighten it. They cannot be buckled when assembled in a jar, as they are simply held in place by the sides of the jar.

On account of the very low internal resistance of the cell, its voltage on charge is low and on discharge is quite high, and as it does not gas until practically charged, a very high efficiency is attained. The ability of a cell to absorb current rapidly on charge is practically proportional to the surface exposed or to its ability to give off current on discharge. For this reason a battery of this construction allows very high charging rates especially at the beginning of the charge.

SUMMARY.

The performance of this battery based on the amount of lead and active material varies from 50 to 200 percent above that of the standard types. The higher percentages prevail at exceedingly high rates and at very low temperatures. The battery is machine made and a large decrease in cost of production has resulted. The batteries are not subject to the mechanical defects and the variability experienced with present standard types.

It has been found practical to ship charged elements as shown in Figure 1, wrapped in paper, to service stations for rebuilding batteries where the container is in good condition. This is due to the fact that the separators which hold the electrolyte like a lamp wick do not allow the plates to dry out any more than when immersed in electrolyte. By this system, a complete battery may be rebuilt in less than an hour at approximately one-half the regular cost. This unusual principle is made use of where a non-spill battery is required, by simply pouring out the excess acid when the battery is in use and replacing it while recharging. There is practically no decrease in capacity when this is done.

Since the life of a battery is practically always destroyed by buckling plates and short circuiting or by the washing off of the active material and since neither of these conditions are possible with the Hazelett Storage Battery, very long life would be expected. Conservatively speaking, their life is averaging from two to three times that of the standard types.

DISCUSSION.

W. E. HOLLAND[1] (*Communicated*): Mr. Hazelett makes some very broad statements regarding his battery, but unfortunately he has not taken the trouble to present actual data and curves obtained on test. A Hazelett three-cell starting-and-lighting battery was obtained for test in December, 1920, by the company which the writer represents. This battery was dated 11-15-20 and bore the type marking "620". The plates were 5⅝ inches wide by 4¾ inches high by about 1/32 inch thick. Each cell had 10 positive and 10 negative plates, which were separated by the so-called "fiber" separators, which seemed to be nothing more than ordinary blotting paper.

These twenty-plate cells were tested against eleven-plate cells of a standard make having plates of the same width and height and jars of the same size as the Hazelett cells. No advantage was found in the Hazelett cells, size for size, either in voltage or capacity at low and medium discharge rates, so tests were made at very high discharge rates where it was expected that the twenty-plate cells might show a voltage advantage. The following is the voltage comparison at various high discharge rates, the voltages being taken after five seconds discharge in each case.

Discharge Rate	Hazelett 20 plate	Philco 11 plate
100 amperes	1.92	1.96
200 "	1.86	1.85
375 "	1.54	1.66
500 "	1.41	1.53

After six cycles of charge and discharge one of the Hazelett cells showed a reversed voltage very early in the discharge and was cut out for inspection. After two additional cycles the remaining two cells showed signs of short-circuits and reduced capacity and were also taken out. Inspection showed the plates to be buckled very badly so that the corners had cut through the separators. The paper separators were mushy and devoid of mechanical strength. There were numerous short-circuit connections through the separators in all cells. It was obvious why the capacity and voltage of the cells had fallen off, in fact it was hard to under-

[1] Research Engineer, Philadelphia Storage Battery Co., Philadelphia, Pa.

stand how any cell could have shown any capacity whatever on the cycle or two just preceding the inspection. The points of connection between positive and negative plates must have had very high contact resistance.

During the war batteries having these extremely thin plates were developed and built by several of the large storage battery companies for the U. S. Signal Corps. These batteries had thin wood separators rather than paper separators. Such batteries were used in airplane service where light weight was all-important and where battery life and cost were almost negligible factors. The Signal Corps was satisfied with a battery life of only 25 cycles, and batteries of such construction fulfilled the requirements very well during this extremely short life-period. Such batteries have not been found economical or practical, either to manufacture or to use, for ordinary peace-time purposes.

C. W. Hazelett (*Communicated*): There are several things which require attention in Mr. Holland's statement. He mentioned he received one of our batteries dated 11-15-20 with the type marked 620. This battery could not have been built at our factory, as we have never used any such markings or dates on our product, although no doubt same was built from elements furnished by us.

He refers to the so-called fiber separator appearing to be nothing but blotting paper, which is not far from the truth. Possibly he is acquainted with the technical product known as sulphite fiber, from which these separators are made.

He reports some rough tests in competition with the Philadelphia battery, in which there was a slight advantage in voltage at high rates of discharge. From what he said in regard to the condition of these cells, I am very much surprised that the comparison was as good in our favor as he shows.

From his statement regarding the condition of the cells on inspection, there is no doubt but that the cells had been overheated to destruction, as this is the only condition that could even approach what he mentions, and which is the standard method of disposing of competitors' batteries in comparative tests.

He remarks of their numerous short circuit connections through the separators in all cells. We have many thousands of these

batteries in service which are from a year to a year and three-quarters old, and, in spite of numerous difficulties which we have had and overcome, the writer has never seen any condition in practice such as Mr. Holland mentions.

I can only explain this by referring to a difficulty we had at one time with the production of a colloid salt of lead which treed directly through and around separators of any and all materials, whether it was wood, rubber or wood fiber.

I might say that every technical reason of the slightest importance why the performance and life of our battery is superior is covered in a paper publication by Mr. James Skinner, of the same company with which Mr. Holland is connected, and given before the Electric Vehicle Association on February 25, 1913.

We realize what Mr. Holland says in his last paragraph that such batteries "have not been found economical or practical to manufacture" has been true until recently, however, at this time they are being manufactured in ever increasing quantities.

A paper presented at the Thirty-ninth General Meeting of the American Electrochemical Society, at Atlantic City, April 23, 1921, President Landis in the Chair.

MARSH ELECTROLYTIC CELLS FOR CHLORINE, CAUSTIC SODA AND HYDROGEN.[1]

By C. W. Marsh.[2]

Abstract.

Description of a high capacity cell for electrolysis of brine, containing graphite anodes, corrugated sheet steel cathodes, with asbestos paper diaphragms clamped tightly to the edges of the cathodes. Arrangements are made for collecting both chlorine and hydrogen. Single cells are made to take up to 5,000 amperes. The ampere efficiencies over long periods amount to 90 percent; the power efficiencies 50 to 65 percent. [J. W. R.]

Recent economic conditions in the United States have greatly influenced the tendency of engineering practice in almost every industrial undertaking. American engineering emphasizes the importance of saving labor. The tendency is to build machines of large capacity, of reasonable efficiency and small bulk. European engineering practice emphasizes the importance of saving power and material. As a rule, machine capacities are smaller and efficiencies higher than in American practice.

In some of the later industrial developments, such as the electrochemical industry, engineering practice in America is a compromise. In the electrolytic alkali industry, with few exceptions, the equipment consists of a large number of units of small or more moderate capacities operating at low but reasonable power efficiencies. Most of the larger plants are the result of many extensions due to the gradually increasing demand. Whether the equipment is typically American or not, electrolytic cells have remained about as small in capacity as in the original installations.

[1] Manuscript received March 12, 1921.

[2] Consulting Engineer, New York City.

In cases where the engineering has followed European practice and design, very large areas of floor space are required. This is due largely to the fact that these cells are of the horizontal type using either mercury cathodes or horizontal diaphragms. In cases where the capacities are of moderate size, the cells are of very large bulk.

It may be interesting to note one exception where the American practice has been strictly followed. The writer designed, built and developed, in co-operation with several distinguished scientists and chemists, the largest electrochemical plant in the United States and one of the most successful. The cells were increased in capacity because it was realized that in large plants, in order to control properly the operations, units must not be too numerous otherwise the necessary chemical control would be too expensive. Not only have the capacities of the units in this plant been increased but part of the equipment is made up of Marsh cells of the type of earlier patents, which greatly increased the power efficiency and which are relatively small in bulk. These cells operate at approximately 5,000 amperes (90 amperes per square foot of cathode surface = 1,000 amperes per square m.) at an average voltage of 3.8, (two months to two and one-half months without change of diaphragm and eight months on anodes) and power efficiencies of 57 percent. About 14.5 tons of caustic is produced daily with these cells and they have been operating continuously for about seven years.

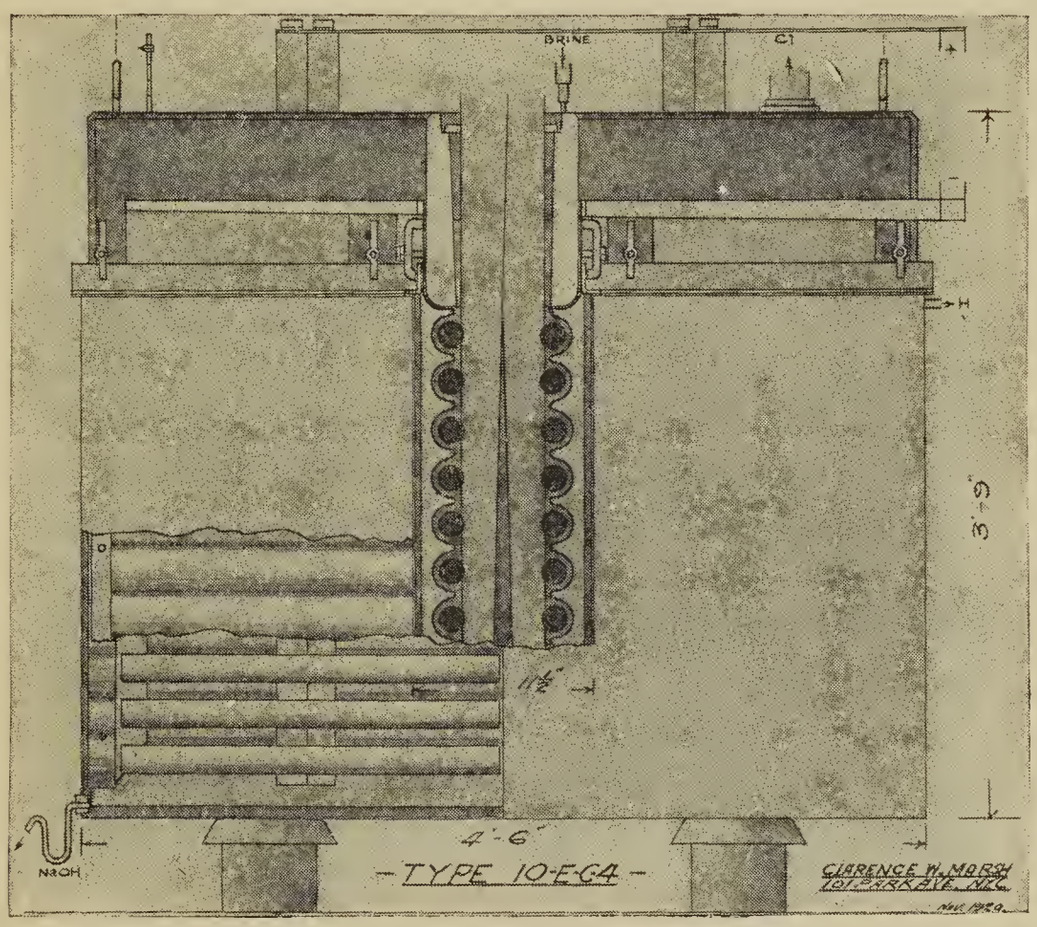
DESCRIPTION OF THE CELLS.

The cell consists of three parts. A structural top with downward extended ends; anodes suspended from the top and a cathode clamped to the top and ends forming the electrolyte compartment. The cell is supported from the top in a box or on insulated beams or suspended from the top through insulated bolts inserted in the top. A hoist operating from an overhead trolley beam or any similar overhead device is used for assembling the cell and to raise and lower the cell into position.

The structural top is like an inverted trough with downward extended narrow ends. The material may be stoneware, reinforced concrete or other suitable material. Openings are pro-

vided in the top for brine inlet and automatic brine control device, brine level indicator, brine gauge glass, chlorine outlet, cleaning holes and openings through which extend the top of the anodes.

The graphite anode consists of four, six, ten or any reasonable number of 1.75 inches (4.4 cm.) diameter graphite rods 24 inches (60 cm.) long arranged one above the other with spaces between and pinned to a rectangular section of graphite acting both as a



Marsh Electrolytic Cell; 1250 Amperes.

support and a leading-in post. Pairs of these anodes are suspended from the top through clamps on the upper ends of the graphite posts.

The cathode consists of perforated sheet steel horizontally corrugated to conform to the surface of the horizontal graphite rods. The asbestos paper diaphragms are laid on the cathodes conforming to corrugations. The cathode is then clamped along the bottom edges of the top and against the ends with the diaphragm acting as a gasket. The cathode and the ends and top

thus form the electrolyte compartment. The chlorine gas collects in the top above the brine. The caustic liquor forms on the cathode and is collected in the supporting box or by other trough-like receivers. The hydrogen gas may be recovered for use by confining the cathode in an enclosure, if the cell is suspended, or within the supporting box. The connections for electric current and for other purposes are made in the usual way. All connections are made along the top of the cell.

Batteries of these cells are made up of a series of cell units in adjoining insulated compartments in a box-like structure. The battery can be placed in any convenient location and is structurally complete.

RECENT IMPROVEMENTS

During the past five years, the writer has patented and developed batteries of 70 percent power efficiency of comparatively small bulk with capacities ranging from 50 to 5,000 amperes. By this latest design larger electrode surfaces than ever are available in a very small space. At normal ratings these cells operate at as low as 35 to 40 amperes per square foot (390 to 440 amperes per square m.) which with the other features permit of power efficiencies of 65 to 73 percent, or an average of 70 percent. These high average power efficiencies are for long periods covering six months' life of diaphragms and about two years' life of anodes. In addition to this, these units become very flexible in that current densities need only be increased to 70 to 80 amperes per square foot, (770 to 880 amperes per square m.), thus doubling the capacities. In this way units up to 10,000 amperes are provided.

It is quite apparent that many important advantages to the electrolytic alkali industry are obtained. The flexibility of the cells is such that during great industrial activity no additional investment need be made except for power-generating equipment to carry the additional load.

The fundamentals of the design have been described in my United States Patent No. 1302824 and in European patents. Other patents are pending. The design and advantages have been described in recent issues of chemical publications, as for instance,

in the *Chemical Age,* (American), January, 1921, and the Canadian *Chemistry and Metallurgy,* February, 1921.

The advantages to the various consumers and manufacturers of chlorine, caustic soda and hydrogen in making these products cheaper will be most apparent in the brief outline of the applications to the smallest as well as to the largest plants. The prevailing idea of a large separate plant or an adjoining electrolytic plant should be discarded. The cells are like storage batteries, compact and of small bulk. They are arranged in battery boxes taking but small space. The smaller capacities are charged or supplied with direct current in the same manner as in a public or private garage. The operation and control is even more simple. In most cases these batteries can be placed in some out of the way corner or in a space adjoining a common alleyway. The following is a brief description of how the various needs are met in a practical and efficient manner.

FOR LABORATORY AND COMMERCIAL INVESTIGATIONS.

Batteries of 50 to 100 amperes and operating at rated capacities average three volts with a power efficiency of 70 percent. The current density is 37 amperes per square foot (400 amperes per square m.) of cathode. These batteries are operated from the usual storage battery charging equipment such as small motor-generator sets and mercury rectifiers.

A battery of 15 cells of 100 amperes capacity takes a floor space of 2 x 12 feet (0.6 x 3.6 m.) Each cell measures 6⅝ in. (16.5 cm.) wide x 15½ in. (39 cm.) long x 22 (55 cm.) high. It produces four pounds (1.8 kg.) of chlorine per hour, 4.5 pounds (2.0 kg.) of caustic soda per hour, 0.11 pound (0.05 kg.) hydrogen per hour. This battery may be operated at double the rated capacity or 200 amperes; each cell absorbs an approximate voltage of 3.9 volts and double the output is obtained for cases of emergency or during excessive demand.

FOR WATER, SEWAGE AND WASTE PURIFICATION AND SMALL INDUSTRIAL AND CHEMICAL PLANTS.

Batteries 100 to 300 amperes operating at three volts average with power efficiencies of 70 percent are recommended. The current density is 37 amperes per square foot (400 amperes per

square m.) when operated under normal conditions. A battery of 15 cells of 300 amperes takes a space of 3 feet wide x 17 feet long (0.9 x 5.1 m.) Each cell measures 10 inches wide x 2 feet 4¾ inches long x 2 feet 8 inches high (25 x 72 x 80 cm.) Each battery produces 12 lb. (5.5 kg.) of chlorine per hour, 13.5 lb. (6.1 kg.) caustic soda per hour, 0.33 pound (0.15 kg.) hydrogen per hour. This battery may be operated at double the rated capacity or 600 amperes, each cell at a voltage of 3.9 volts, in which case double the output is obtained.

Under normal conditions the batteries operate six months and longer without interruption of the current for the purpose of changing diaphragms. The anodes last two years without change. A part of the anodes lasts much longer. The renewals are made in place through labor-saving devices which are a part of the batteries. The anodes are not disturbed when the diaphragms are changed and little physical effort is necessary for lifting or making these changes. Chlorine, under these conditions, for small plants with electrical power at two cents per kw. hr. and with salt and caustic soda wasted, will cost at the present price level approximately eight cents per pound. This is a considerable saving over liquid chlorine under the same conditions at 12 cents per pound and for available chlorine in bleach at a much higher figure. Under lower price conditions the difference in cost will be proportional. However, in these cases as well as for other plants, the local conditions will usually permit of a ready sale of the caustic liquor, which contains a large amount of salt, to soap makers, textile concerns, laundries and other industrial concerns. The caustic liquor solution should not be wasted, as it is worth, under present conditions approximately 3 to 3.5 cents per pound of caustic soda content and there is produced 1.1 pounds (0.5 kg.) for each pound (0.45 kg.) of chlorine. With this credit, which can be obtained with a little effort, the cost of chlorine may be reduced to 4.5 or 5 cents a pound and under.

The only labor required other than the electrical control of the current by hand according to the output required, is making the pure brine. The salt is dissolved, the impurities precipitated with soda ash and caustic liquor; the brine filtered and neutralized with acid. This can be done once a month in the smallest plants

or once a week in the larger plants. One or two cheap wooden tubs are sufficient. The amount of brine to be made up is small. The chlorine output is regulated electrically by hand by changing the charging rate of the batteries. Batteries can be charged at one-half or double the normal rate, giving a wide range of output to meet the requirements of a small plant. At the low rates, there will be a waste of salt unless it is recovered or sold which will be counterbalanced by the saving of power as the power efficiency will increase due to the lower voltage. At the higher rate the waste of salt becomes less but the power cost will become higher as the power efficiency will drop off on account of the higher voltage due to increased current density. The equipment cost will be about the same as the cost of liquid chlorine control apparatus plus the working capital needed for a stock of liquid chlorine in cylinders. In some cases the cost may be lower.

FOR DYE HOUSES, MANUFACTURING INTERMEDIATES, SMALL PULP AND PAPER MILLS, TEXTILE MILLS, ETC.

Batteries of 300 to 600 amperes, each cell averaging three volts and 70 percent power efficiency, are recommended. Standard electrochemical motor-generator sets are used in these cases.

A battery of 15 cells of 600 amperes will take a space of 5x17 feet (1.5x5.1 m.) Each cell measures 10 inches x 4 feet 5½ inches long x 2 feet 8 inches high (25x134x80 cm.) This battery will produce 24 pounds (11 kg.) of chlorine, 27 pounds (12.3 kg.) of NaOH, and 0.66 pound (0.3 kg.) hydrogen per hour. The current may be raised to 1200 amperes and double the output obtained. The voltage will increase to approximately 3.9 volts per cell.

In some cases, the hydrogen can be used as well. For instance, hydrochloric acid can be made in small combustion furnaces. Pure hydrogen for the hydrogenation of oils can be produced cheaper than by the oxygen-hydrogen electrolytic cells if the chlorine and caustic soda is used or sold.

In most dye houses and in other plants a large amount of salt is used and no greater expense is involved in taking care of the additional requirements for salt. Supplies of purified brine can be made up each week, or daily in large plants, in a few wooden

tubs. The accidental escape of large amounts of chlorine will not occur as the batteries make the chlorine as required without the necessity of storage. Throwing off the current will stop the gas.

FOR LARGE ELECTROLYTIC ALKALI, BLEACH, AND LIQUID CHLORINE PLANTS, AND FOR LARGE BLEACHED PULP AND CHEMICAL INSTALLATIONS.

Batteries of 1,250 to 5,000 ampere cells connected up in series are recommended. During periods of intensive demands these batteries can be operated at double capacity and then batteries of 2,500 to 10,000 amperes are available. The electrical generating equipment can be coupled in multiple for this extra demand, using spare machines. The advantages of such a flexible arrangement have been referred to. There is no necessity of large companies carrying the burden of idle equipment during periods of industrial inactivity. This is an immense saving aside from the interest on the money. The depreciation of idle equipment is two or three times that of equipment kept in good repair and actually in use. This is especially true in the electrochemical industry.

The individual Marsh cells measure 10 inches wide x 4 feet 5½ inches long (25 x 134 cm.) for the 1,250-2,500 ampere cells to 16 feet 8 inches long (5m.) for the 5,000-10,000 ampere cells; a battery of 15 cells can be accommodated in a battery box 16 feet 8 inches (5 m.) long. The average cell voltage for these cells at rated capacities is 3.35, with power efficiency of 63 percent. At double rated capacity the voltage will be a little over four volts, giving 50 percent power efficiency.

The ampere efficiencies will vary according to the conditions under which the cells operate. With saturated electrolyte or with circulated brine the efficiences will be 95 to 97 percent for shorter periods of operation. Without saturated electrolyte or circulation of brine, which is an additional expense, the ampere efficiency will be about 92 percent for the shorter operating periods. For long operating periods, six months or more, the ampere efficiency will amount to approximately 90 percent. This would be the normal condition for these cells, as there is no necessity for changing the original diaphragms at less intervals than six months. It is under-

stood that normal conditions include a proper percentage of NaOH in the caustic soda liquor, 8 to 12 percent. Ampere efficiencies will always drop if the NaOH percentage varies from these limits.

The power efficiencies stated for the installations referred to above are average power efficiencies, and have been based on 90-92 percent ampere efficiency and not on 95-97 percent ampere efficiency. In case the extra cost for saturated brine is warranted, the power efficiency will be higher.

The extremely low average voltage of the Marsh cell is the result of the ability to furnish large electrode surface within a small space by the use of separate horizontal anode members and corrugated cathodes, and at the same time maintain a minimum resistance between the electrodes by constantly removing the chlorine and keeping the surfaces in close relation. Twice the usual depth of cathode can be used without increasing the voltage over that of a reasonable minimum. The chlorine is deflected at frequent intervals in the height of the cathode to the back of the superimposed anode members. The cheap asbestos paper diaphragms are held in place at frequent intervals in the height. The deposits on the diaphragm, especially the wasted graphite, are distributed regularly without clogging the passages for the electrolyte. The circulation is unusually good. The space between the electrodes is an absolute minimum. The corrugated cathode maintains its shape better than flat cathodes of thin metal which bulge out of shape. It is impossible to obtain an absolute minimum space with thin flat plates without great expense. The removal of the accumulation of chlorine bubbles between the electrodes is very effective.

These conditions together with the 50 percent added surface per unit of height makes it possible to build small cells of large capacities at a reasonable cost and obtain cells that will operate at the highest power efficiencies that can be obtained in any cell no matter how much money is spent to obtain this desirable end.

In electrolytic cells other than Marsh design the highest commercial average power efficiencies, of 63-70 percent for long periods of time (six months without changing diaphragms and about two years without changing any part of the anodes) can

only be obtained at prohibitive cost of installation and operation. That is the reason cells are not operated at these high power efficiencies at the present date. The dimensions of the cells of reasonable working capacities would be too great. They would take too much space and at enormous cost for buildings. The capacities would be relatively low or would be operated for short periods of time with frequent renewals of diaphragms and anodes, thus involving great expense.

Data of Marsh cells are available to parties interested and show power savings amounting to one-sixth or more, depending on the length of run. Graphite expense is cut in half. Every other item of expense in operating cells is decreased because the power heretofore largely wasted in heating up cells and destroying graphite, cell bodies, and cathodes, is now conserved to the extent of one-third to one-half of the wasted power. Destruction and secondary reactions go hand in hand with high voltage as shown in actual commercial practice. Large capacity cells have been obtained by operating at high current densities but at the sacrifice of power, graphite and other raw material costs.

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